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(54) Title: ORTHO SUBSTITUTED CHIRAL PHOSPHINES AND PHOSPHINITES AND THEIR USE IN ASYMMETRIC CATAYLTIC REACTIONS

(57) Abstract: 3,3'-substituted chiral biaryl phosphine and phosphinite ligands and metal complexes based on such chiral ligands useful in asymmetric catalysis are disclosed. The metal complexes are useful as catalysts in asymmetric reactions, such as, hydrogenation, hydride transfer, allylic alkylation, hydrosilylation, hydroboration, hydrovinylation, hydroformylation, hydroformylation, olefin metathesis, hydrocarboxylation, isomerization, cyclopropanation, Diels-Alder reaction, Heck reaction, isomerization, Aldol reaction, Michael addition, epoxidation, Kinetic resolution and [m+n] cycloaddition. The metal complexes are particularly effective in Ru-catalyzed asymmetric hydrogenation of beta-ketoesters to beta-hydroxyesters and Ru-catalyzed asymmetric hydrogenation of enamides to beta amino acids.

ORTHO SUBSTITUTED CHIRAL PHOSPHINES AND PHOSPHINITES AND THEIR USE IN ASYMMETRIC CATALYTIC REACTIONS

BACKGROUND OF THE INVENTION

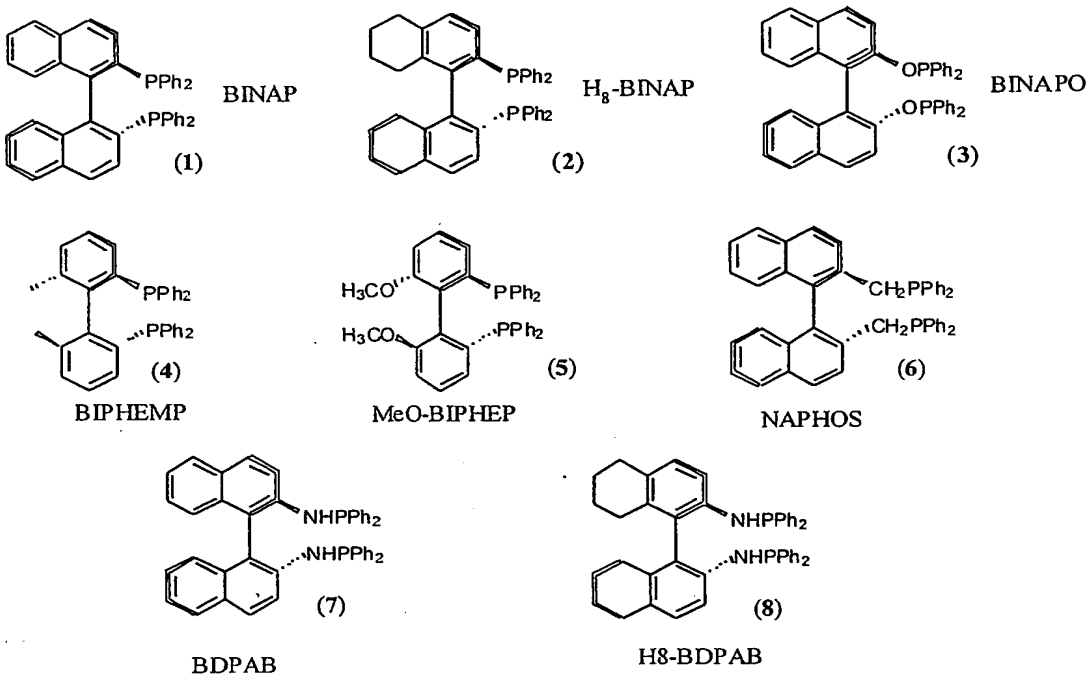
1. FIELD OF THE INVENTION

The present invention relates to novel chiral ligands derived from 3,3'-substituted biaryl phosphines and phosphinites. More particularly, the present invention relates to transition metal complexes of these chiral phosphine ligands. The transition metal complexes are useful as catalysts in asymmetric reactions, such as, hydrogenation, hydride transfer, allylic alkylation, hydrosilylation, hydroboration, hydrovinylation, hydroformylation, olefin metathesis, hydrocarboxylation, isomerization, cyclopropanation, Diels-Alder reaction, Heck reaction, isomerization, Aldol reaction, Michael addition, epoxidation, kinetic resolution and [m+n] cycloaddition.

2. DESCRIPTION OF THE PRIOR ART

Discovery of new chiral ligands is crucial in developing highly enantioselective transition metal-catalyzed reactions. Many chiral ligands have been made for applications in asymmetric catalysis, however, relatively few of these chiral ligands are commonly used in industry for the synthesis of chiral molecules.

Several chiral ligands having a biaryl backbone are known in the prior art. These are summarized below:

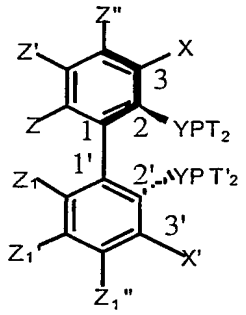


Among these ligands, BINAP (1) is one of the most frequently used chiral ligands. The axially dissymmetric, fully aromatic BINAP has demonstrated to be highly effective for many asymmetric reactions (Noyori, R. et al. *Acc. Chem. Res.* **1990**, 23, 345, Ohkuma, T. et al. *J. Am. Chem. Soc.* **1998**, 120, 13529). Recent results show that partially hydrogenated BINAP with a larger bite angle, H8-BINAP (2), is a better ligand for certain asymmetric reactions due to restriction of conformational flexibility (Zhang X. et al. *Synlett* 1994, 501). Chiral BINAPO (3) was made and it was not effective due to the conformational flexibility (Grubbs, R. et al. *Tetrahedron Lett.* **1977**, 1879). Other axially dissymmetric ligands such as BIPHEMP (4) and MeO-BIPHEP (5) were developed and used for a number of asymmetric reactions (Schmid, R. et al. *Pure & Appl. Chem.* **1996**, *68*, 131; Schmide, R. et al. *Helv. Chim. Acta*, 1988, 71, 897). However, the present inventor is not aware of any examples of related 3,3' substituted chiral biaryl phosphines, the subject of the present invention, being disclosed in the prior art (Broger , E. A. et al., WO 92/16536 and Broger, E. A. et al., WO93/15089).

NAPHOS (6), another example of a prior art compound has been prepared (Tamao, K. et al. *Tetrahedron Lett.* **1977**, 1389) and was found to be not effective for asymmetric hydrogenation reaction. The corresponding ligands with the N linker, BDPAB (7) and H8-BDPAB (8) have also been made and tested for asymmetric hydrogenation reactions (Zhang, F. et al. *J. Am. Chem. Soc.* **1998**, *120*, 5808).

SUMMARY OF THE INVENTION

The present invention includes a ligand represented by the formula or its enantiomer:



wherein each X and X' is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

wherein each Z and Z_1 is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$; or wherein Z and Z_1 together form the bridging group A-B-A_1;

wherein each Z', Z", Z_1' and Z_1" is independently selected from the group consisting of: H, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$; or wherein Z' and Z together form the bridging group A'-B-A; Z' and Z together form a fused

cycloaliphatic or aromatic group; Z_1 and Z_1' together form the bridging group A_1-B_1-A_1'; and/or Z_1 and Z_1' together form a fused cycloaliphatic or aromatic group;

wherein each A, A', A_1 and A_1' is independently selected from the group consisting of: O, CH_2, NH, NR, S, CO and a bond;

wherein each B and B_1 is independently selected from the group consisting of: linear, branched or cyclic alkylene of 1 to 6 carbon atoms, arylene of 6 to 12 carbon atoms, O, CH_2, NH, NR, S, CO, SO_2, P(O)R, P(O)OR, POR, SiR_2 and a bond;

wherein each T is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R", YR', YR", Y'R' and Y"R"; or wherein two T groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

wherein each T' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R", YR', YR", Y'R' and Y"R"; or wherein two T' groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

wherein each R, R' and R" is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, aralkyl and alkaryl of 1 to 22 carbon atoms; or wherein two R groups, two R' groups or two R" group together form an alkylene or arelene group; and

wherein each Y, Y' and Y" is independently selected from the group consisting of: O, CH_2, NH, S and a bond between carbon and phosphorus; with the proviso that when the Y group at the 2' position is a bond between carbon and phosphorus, X' is hydrogen.

The present invention further includes a catalyst prepared by a process, which includes: contacting a transition metal salt, or a complex thereof, and a ligand according to the present invention.

The present invention still further includes a process for preparation of an asymmetric compound including: contacting a substrate capable of forming an

asymmetric product by an asymmetric reaction and a catalyst prepared by a process including: contacting a transition metal salt, or a complex thereof, and a ligand according to the present invention.

The metal complexes are useful as catalysts in asymmetric reactions, such as, hydrogenation, hydride transfer, allylic alkylation, hydrosilylation, hydroboration, hydrovinylation, hydroformylation, olefin metathesis, hydrocarboxylation, isomerization, cyclopropanation, Diels-Alder reaction, Heck reaction, isomerization, Aldol reaction, Michael addition, epoxidation, kinetic resolution and [m+n] cycloaddition. The metal complexes are particularly effective in Ru-catalyzed asymmetric hydrogenation of beta-ketoesters to beta-hydroxyesters and Ru-catalyzed asymmetric hydrogenation of enamides to beta amino acids.

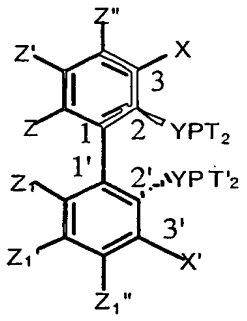
DETAILED DESCRIPTION OF THE INVENTION

The present invention includes 3,3'-substituted chiral biaryl phosphines and phosphinites and related ligands for applications in asymmetric catalysis. Introduction of 3,3'-substituted groups can restrict the rotation of substituents adjacent to the phosphines. Control of orientations of these groups around the phosphine can lead to effective chiral induction for asymmetric reactions. Metal complexes of these phosphines, phosphinites and related non-C_2 symmetric ligands with ortho substitution are useful for a large variety of asymmetric reactions. A number of chiral ligands can be made having the desired structure in which the 3,3' positions are substituted, with the proviso that at least one ortho position is occupied by a group other than H atom.

In the non-C_2 symmetric ligands, ortho substituted groups play an important role for asymmetric catalysis. The 3,3' substituted chiral biaryl phosphines, phosphinites and related ligands of the present invention are

described below. An important feature of these ligands is that at least one of the 3 and 3' positions must be occupied by a group other than hydrogen.

The ligands are represented by the formula:



wherein each X and X' is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

wherein each Z and Z_1 is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$; or wherein Z and Z_1 together form the bridging group A-B-A_1;

wherein each Z', Z", Z_1' and Z_1" is independently selected from the group consisting of: H, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$; or wherein Z' and Z together form the bridging group A'-B-A; Z' and Z together form a fused cycloaliphatic or aromatic group; Z_1 and Z_1' together form the bridging group A_1-B_1-A_1'; and/or Z_1 and Z_1' together form a fused cycloaliphatic or aromatic group;

wherein each A, A', A_1 and A_1' is independently selected from the group consisting of: O, CH_2, NH, NR, S, CO and a bond;

wherein each B and B_1 is independently selected from the group consisting of: linear, branched or cyclic alkylene of 1 to 6 carbon atoms, arylene of 6 to 12

carbon atoms, O, CH_2, NH, NR, S, CO, SO_2, P(O)R, P(O)OR, POR, SiR_2 and a bond;

wherein each T is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R", YR', YR", Y'R' and Y"R"; or wherein two T groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

wherein each T' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R", YR', YR", Y'R' and Y"R"; or wherein two T' groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

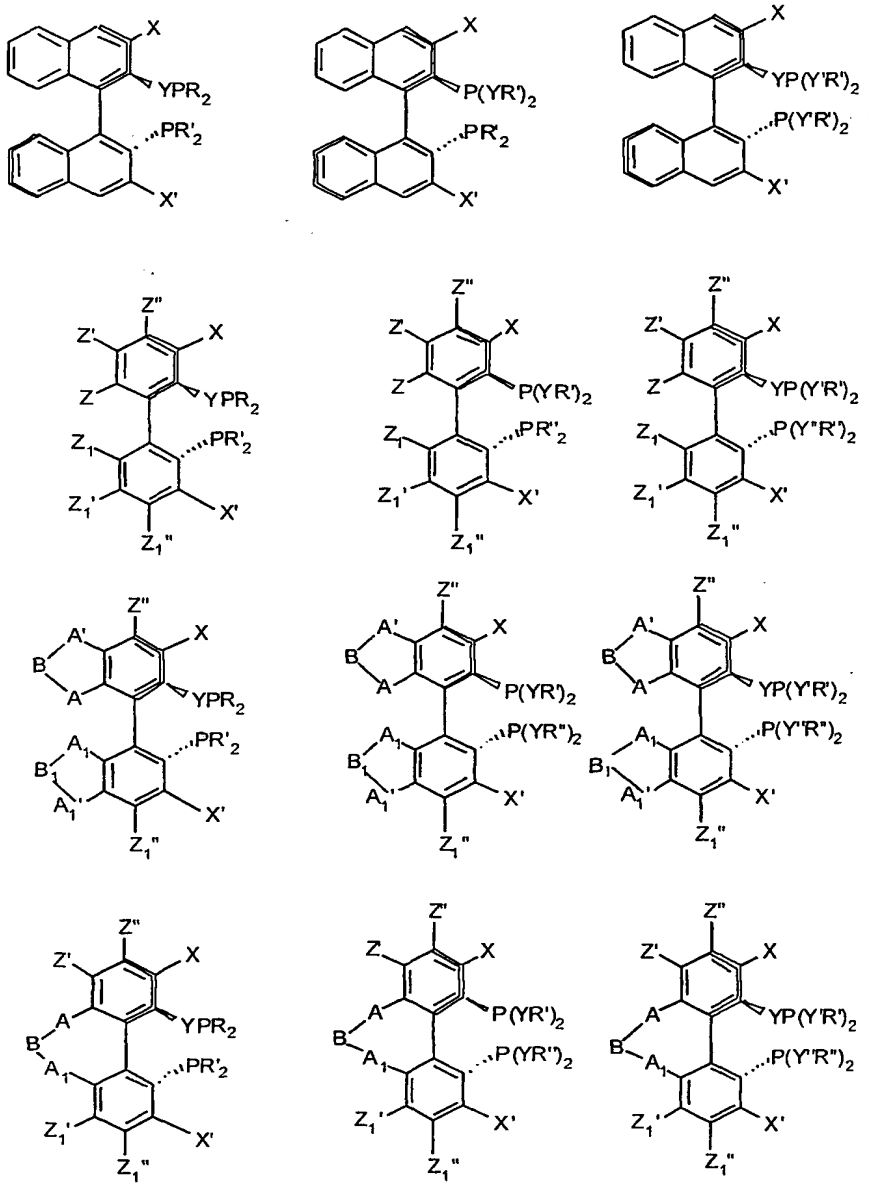
wherein each R, R' and R" is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, aralkyl and alkaryl of 1 to 22 carbon atoms; or wherein two R groups, two R' groups or two R" group together form an alkylene or arelene group; and

wherein each Y, Y' and Y" is independently selected from the group consisting of: O, CH_2, NH, S and a bond between carbon and phosphorus; with the proviso that when the Y group at the 2' position is a bond between carbon and phosphorus, X' is hydrogen. Preferably the alkylene group includes compounds represented by the formula: $-(CH_2)_n-$, wherein n is an integer in the range of from 1 to 8. The present invention also includes the corresponding enantiomer of each of the above ligands.

The substituted alkyl group can have one or more substituents and each substituent can independently be halogen, ester, ketone, carboxylic acid, hydroxy, alkoxy, aryloxy, thiol, alkylthio or dialkylamino. The aryl groups can optionally have one or more substituents, each of which can independently be halogen, ester, ketone, sulfonate, phosphonate, hydroxy, alkoxy, aryloxy, thiol, alkylthiol, nitro, amino, vinyl, substituted vinyl, carboxylic acid, sulfonic acid or phosphine. The arylene groups optionally can have one or more substituents, each of which can independently be halogen, ester, ketone, sulfonate, phosphonate, hydroxy, alkoxy, aryloxy, thiol, alkylthiol, nitro, amino, vinyl, substituted vinyl, carboxylic acid,

sulfonic acid or phosphine. Preferably, each of the arylene groups can be 1,2-divalent phenyl, 2,2'-divalent-1,1'-biphenyl, 2,2'-divalent-1,1'-binaphthyl or ferrocene, i.e., a -Fc- group.

In a preferred embodiment, the present invention includes compounds represented by the following formulas:



wherein each X and X' is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

wherein each Z and Z_1 is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$; or wherein Z and Z_1 together form the bridging group A-B-A_1;

wherein each Z', Z", Z_1' and Z_1" is independently selected from the group consisting of: H, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$; or wherein Z' and Z together form the bridging group A'-B-A; Z' and Z together form a fused cycloaliphatic or aromatic group; Z_1 and Z_1' together form the bridging group A_1-B_1-A_1'; and/or Z_1 and Z_1' together form a fused cycloaliphatic or aromatic group;

wherein each A, A', A_1 and A_1' is independently selected from the group consisting of: O, CH_2, NH, NR, S, CO and a bond;

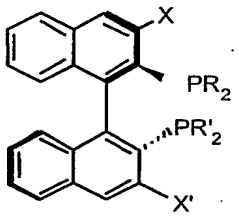
wherein each B and B_1 is independently selected from the group consisting of: linear, branched or cyclic alkylene of 1 to 6 carbon atoms, arylene of 6 to 12 carbon atoms, O, CH_2, NH, NR, S, CO, SO_2, P(O)R, P(O)OR, POR, SiR_2 and a bond;

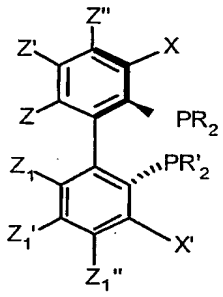
wherein each YR', YR", Y'R' and Y"R" is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide and aryloxide; or wherein two YR', YR", Y'R' or Y"R" groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

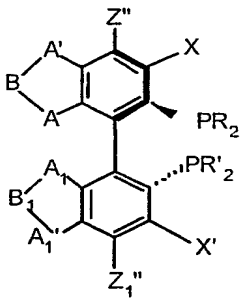
wherein each R, R' and R" is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, aralkyl and alkaryl of 1 to 22 carbon atoms; or wherein two R groups, two R' groups or two R" group together form an alkylene or arelene group; and

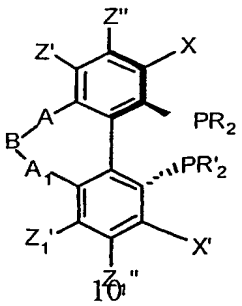
wherein each Y, Y' and Y" is independently selected from the group consisting of: O, CH_2, NH, S and a bond between carbon and phosphorus; with the proviso that when the Y group at the 2' position is a bond between carbon and phosphorus, X' is hydrogen.

In another preferred embodiment, the present invention includes compounds represented by the following formulas:









wherein each X is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

wherein each X' is independently selected from the group consisting of: hydrogen, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

wherein each Z and Z_1 is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

wherein each Z', Z", Z_1' and Z_1" is independently selected from the group consisting of: H, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

wherein each A, A', A_1 and A_1' is independently selected from the group consisting of: O, CH_2, NH, NR, S, CO and a bond;

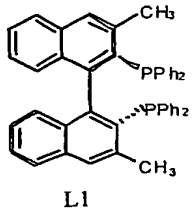
wherein each B and B_1 is independently selected from the group consisting of: linear, branched or cyclic alkylene of 1 to 6 carbon atoms, arylene of 6 to 12 carbon atoms, O, CH_2, NH, NR, S, CO, SO_2, P(O)R, P(O)OR, POR, SiR_2 and a bond;

wherein each R and R' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, aralkyl and alkaryl of 1 to 22 carbon atoms, alkoxide and aryloxide; or

wherein two R groups or two R' groups together form an alkylene, arelene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl groups.

The ligands of the present invention can be a racemic mixture of enantiomers. Preferably, the ligand is a non-racemic mixture of enantiomers, and more preferably, the ligand is one of the enantiomers. Preferably, the ligand has an optical purity of at least 85% ee, and more preferably, the ligand has an optical purity of at least 95% ee.

Selected examples of the chiral ligands according to the present invention are represented by the following formulas:



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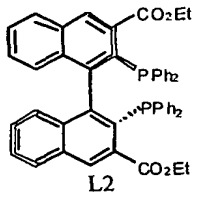

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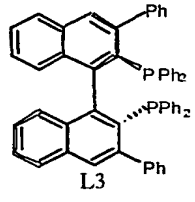

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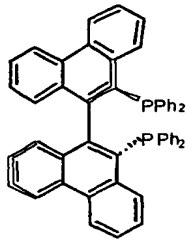

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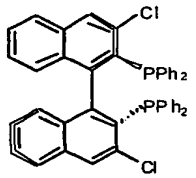

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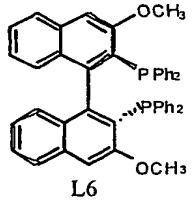
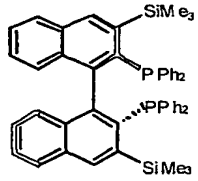


L6



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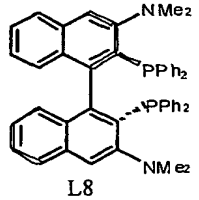
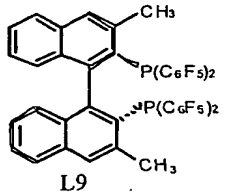
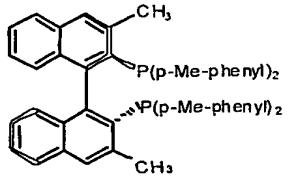


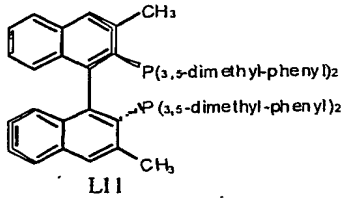
L8



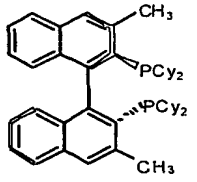
L9



L10



L11



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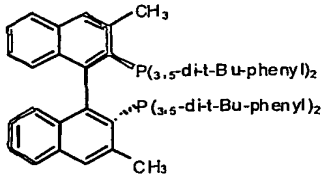

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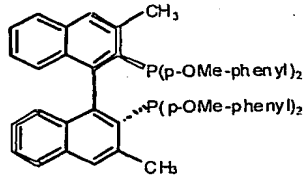

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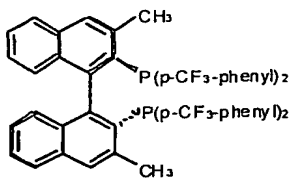

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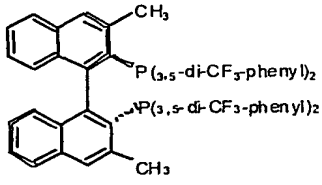

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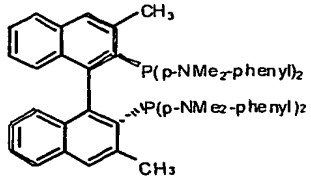

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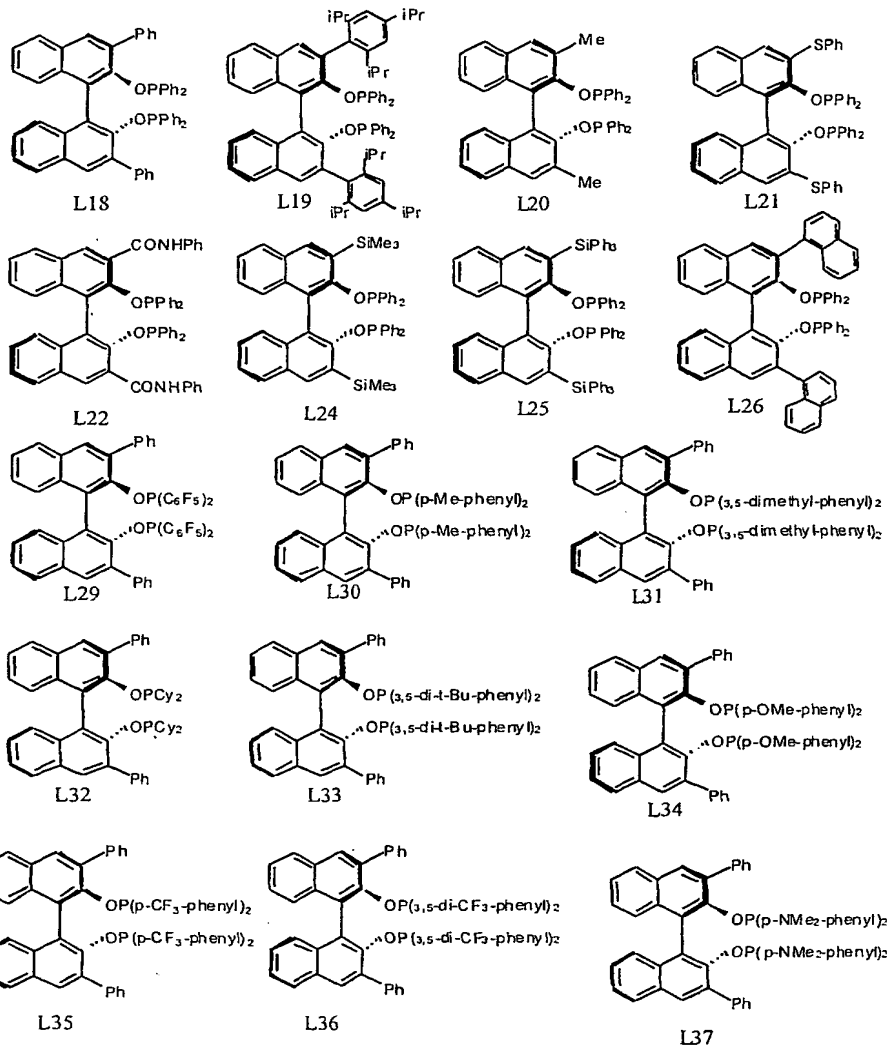

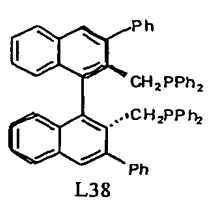

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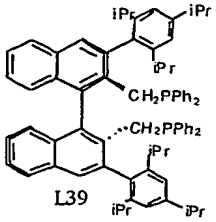

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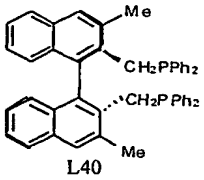

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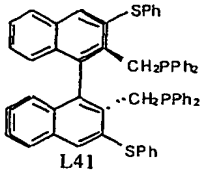

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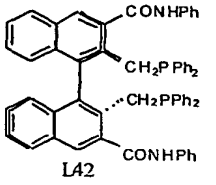

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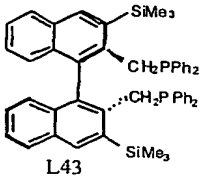

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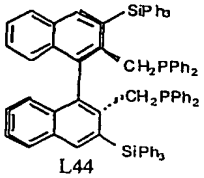

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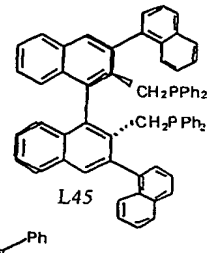

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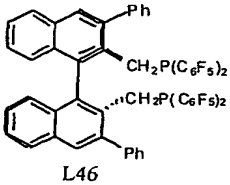

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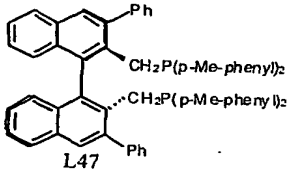

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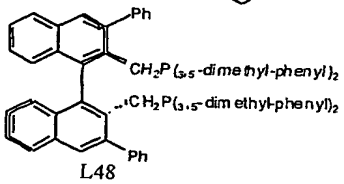

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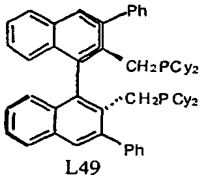

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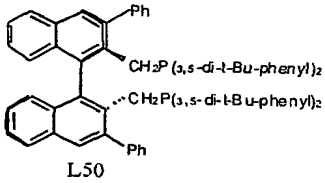

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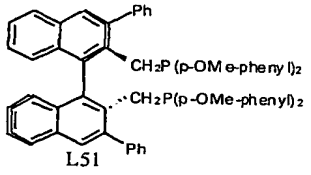

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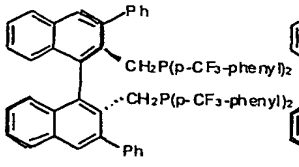

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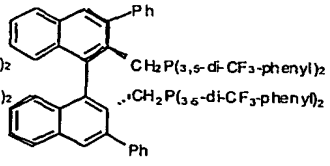

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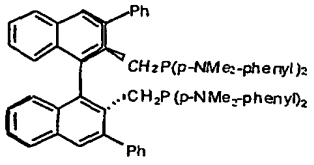

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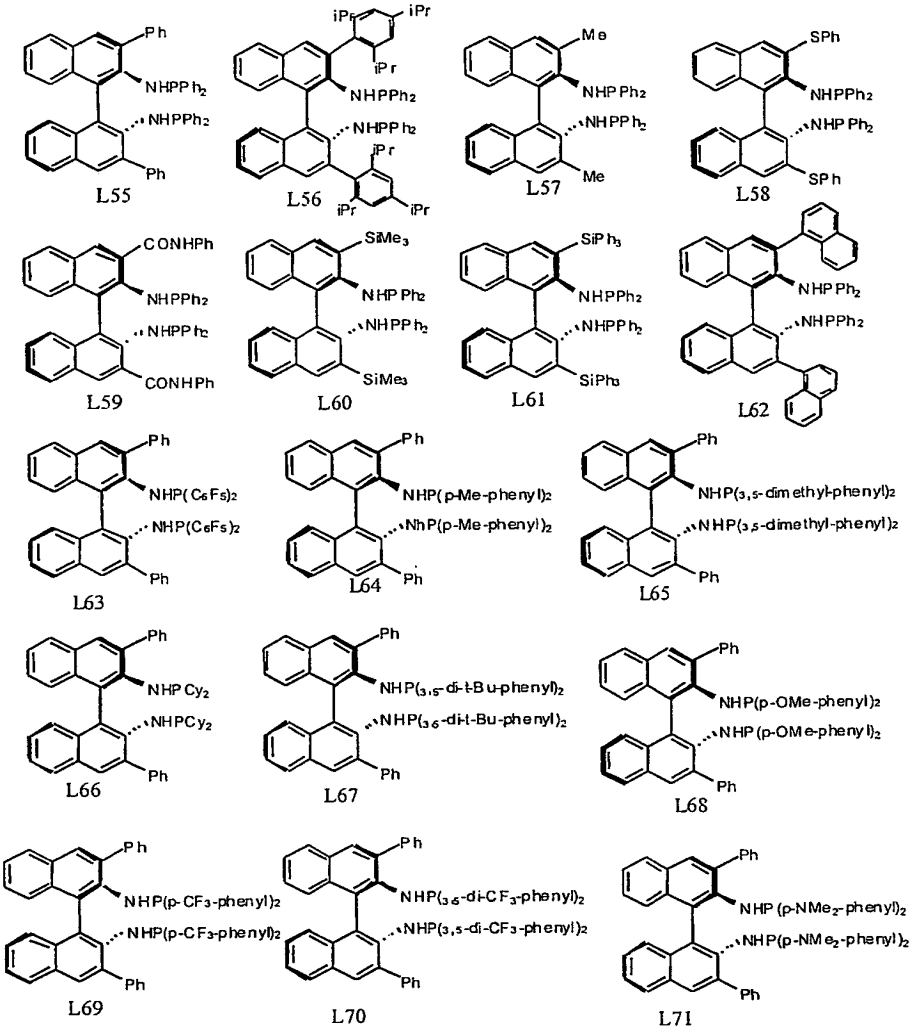

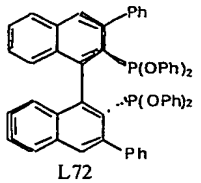
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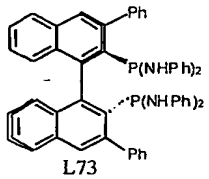
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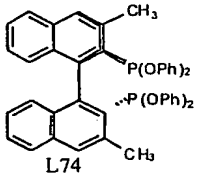
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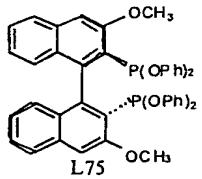
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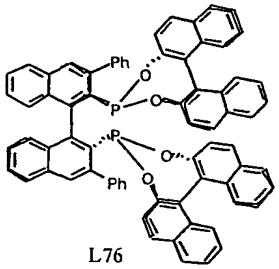
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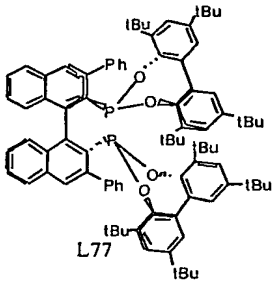
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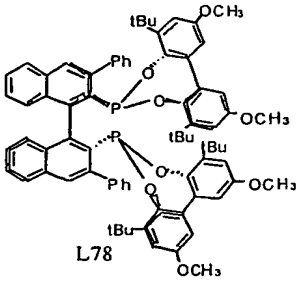
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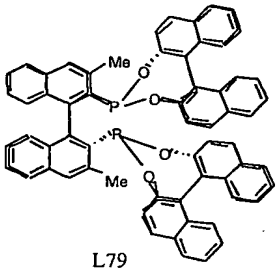
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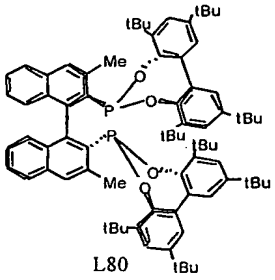
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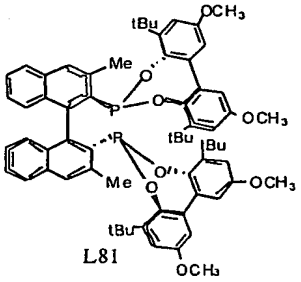
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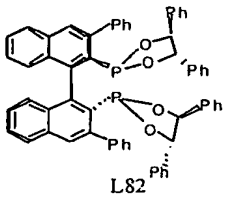
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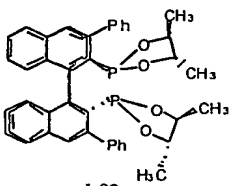
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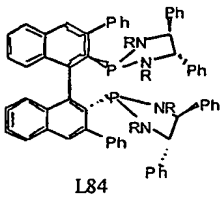
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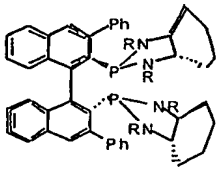
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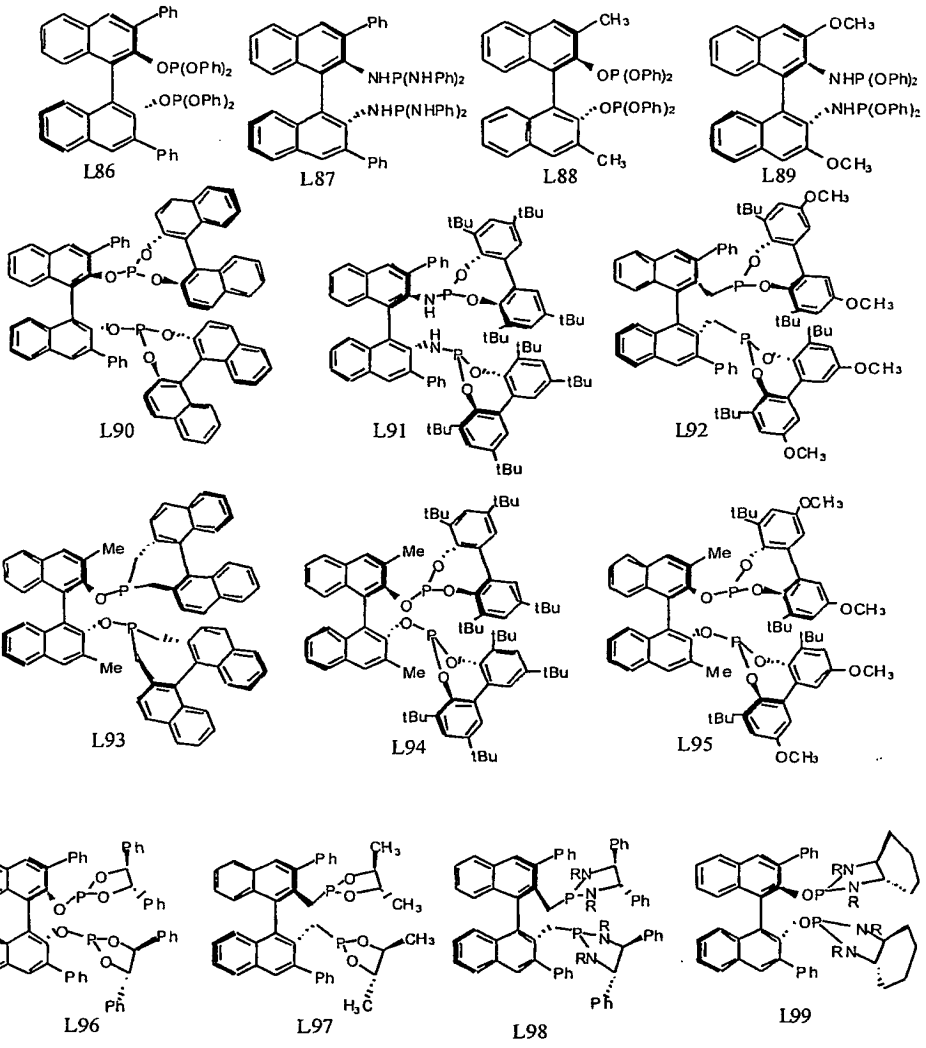

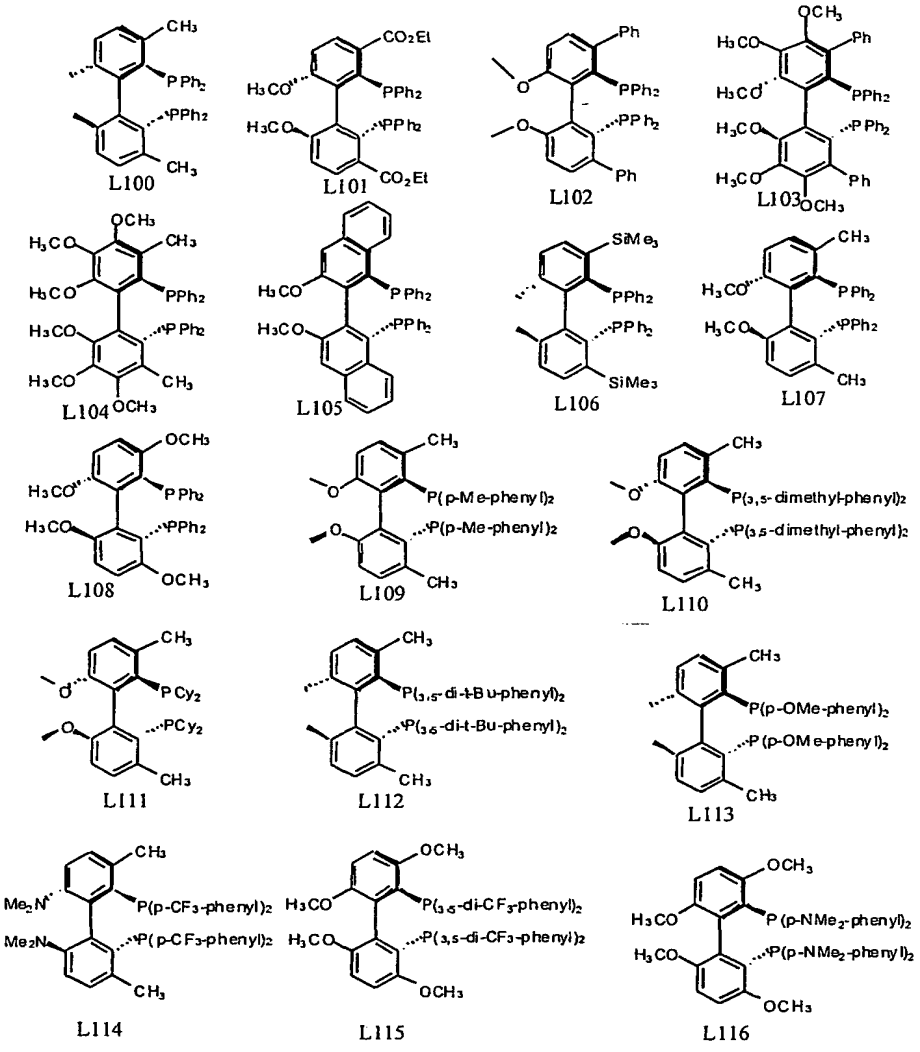

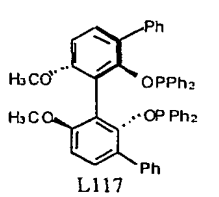

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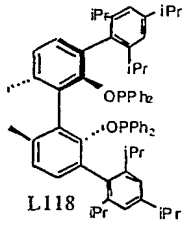

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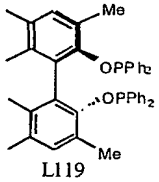

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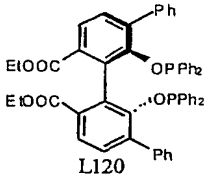

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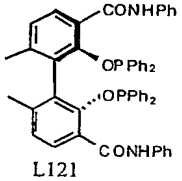

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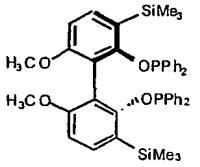

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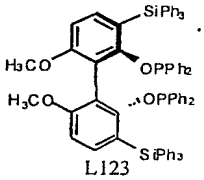

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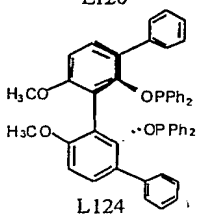

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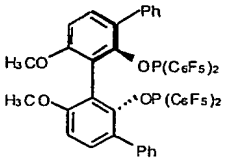

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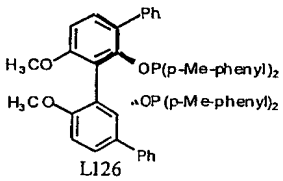

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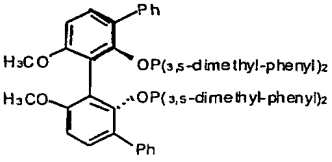

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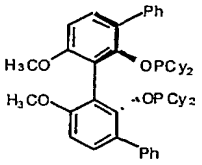

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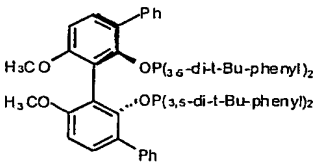

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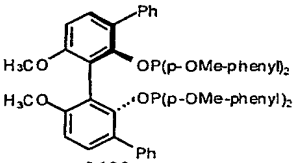

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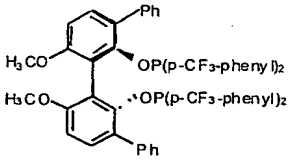

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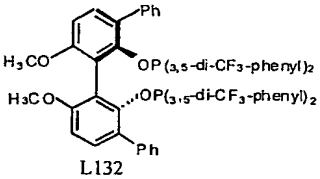

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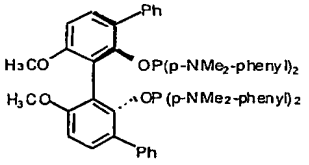

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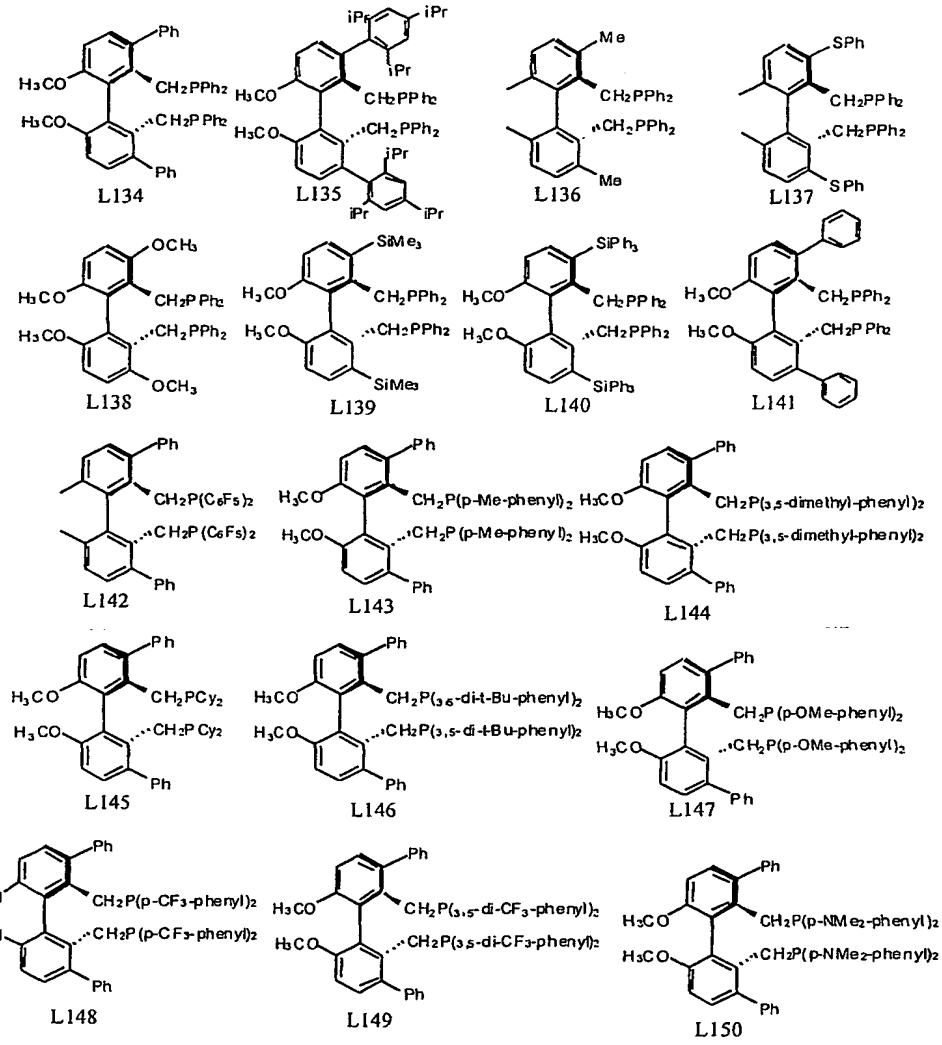

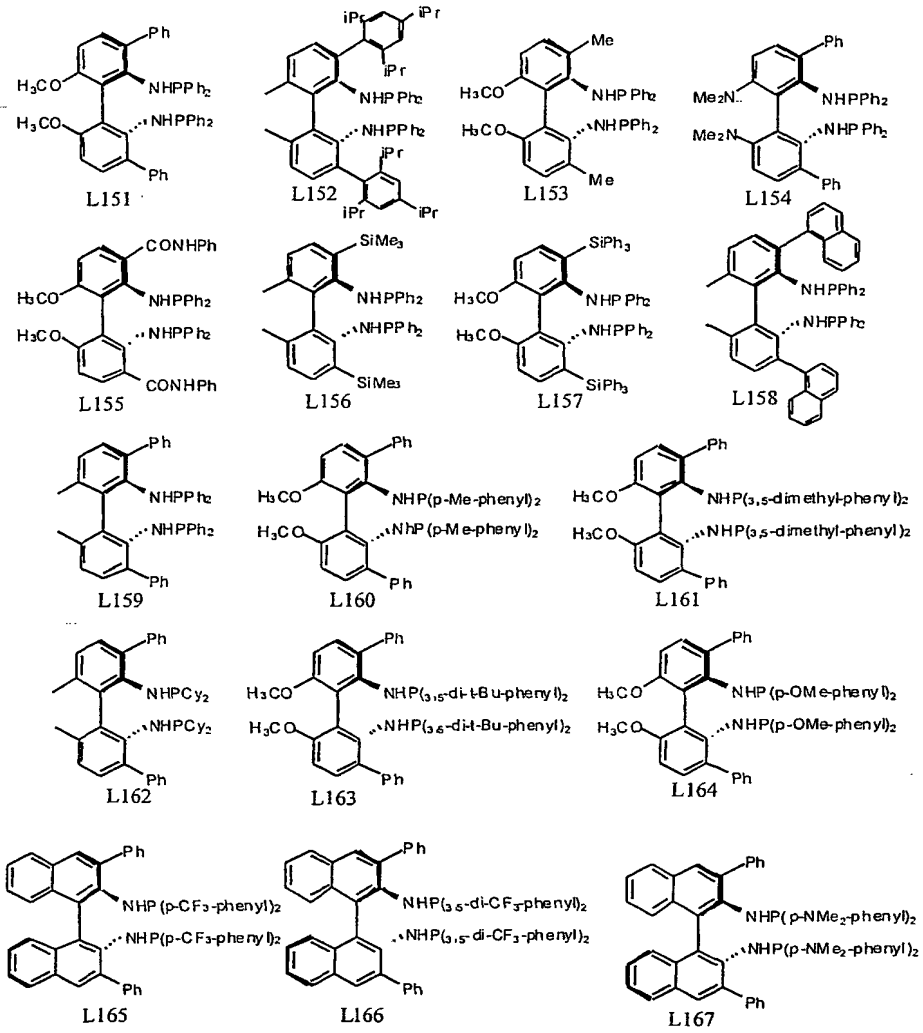

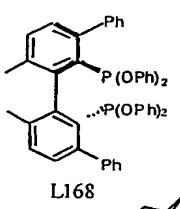
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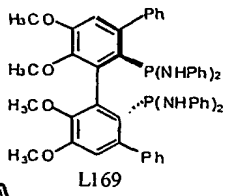
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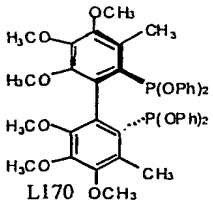
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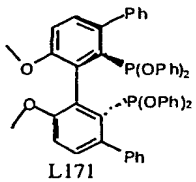
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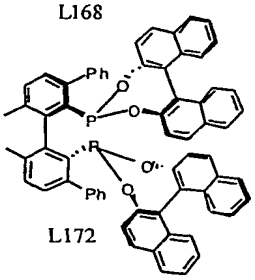
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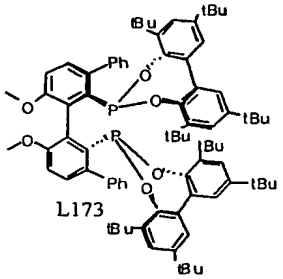
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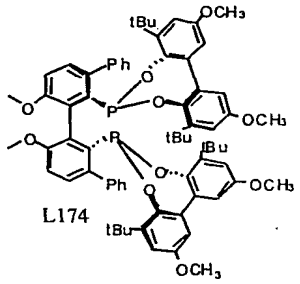
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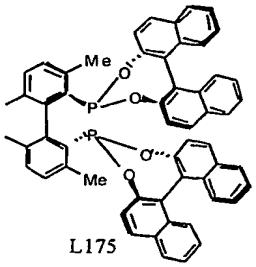
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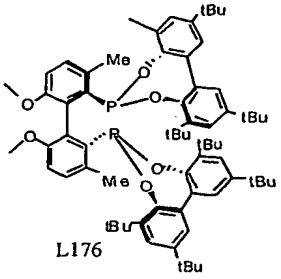
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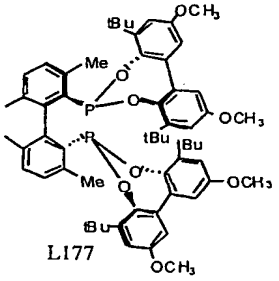
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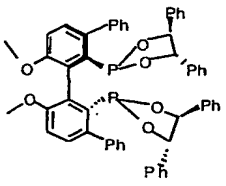
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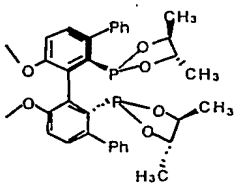
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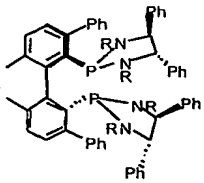
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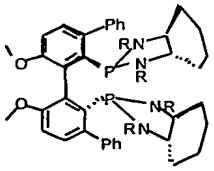
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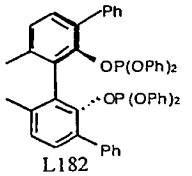
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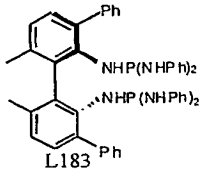
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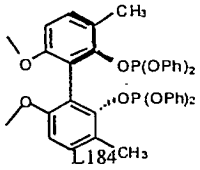
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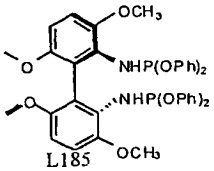
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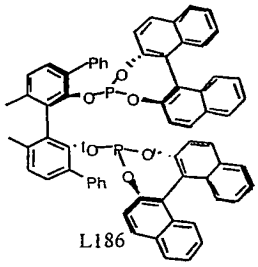
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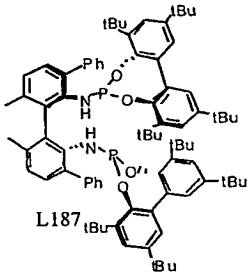
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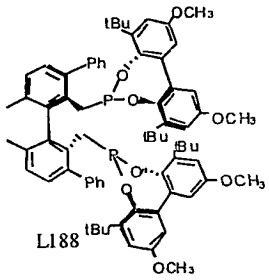
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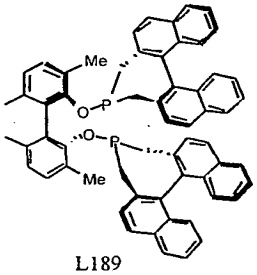
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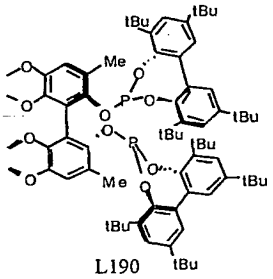
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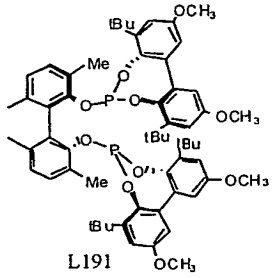
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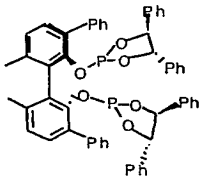
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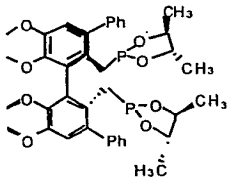
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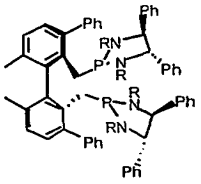
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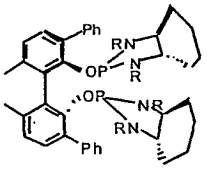
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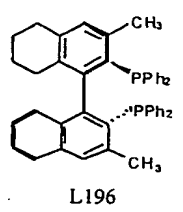

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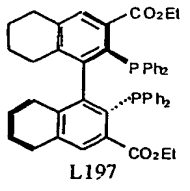

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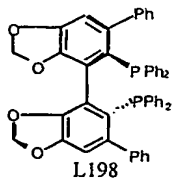

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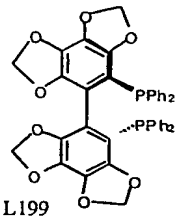

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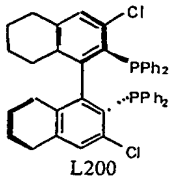

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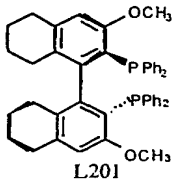

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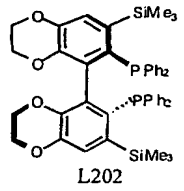

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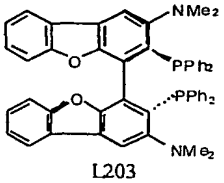

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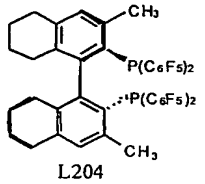

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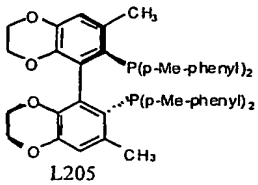

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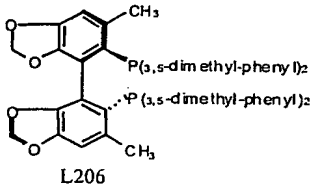

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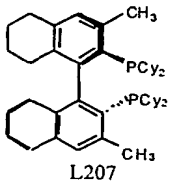

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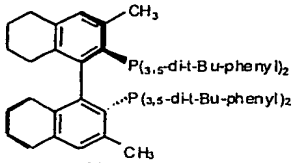

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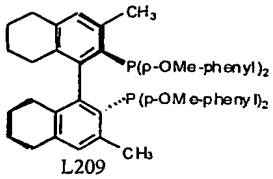

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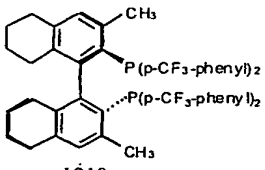

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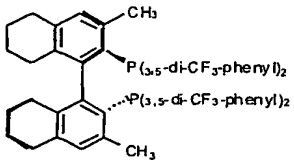

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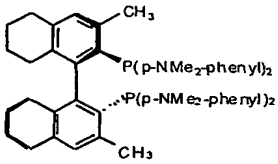

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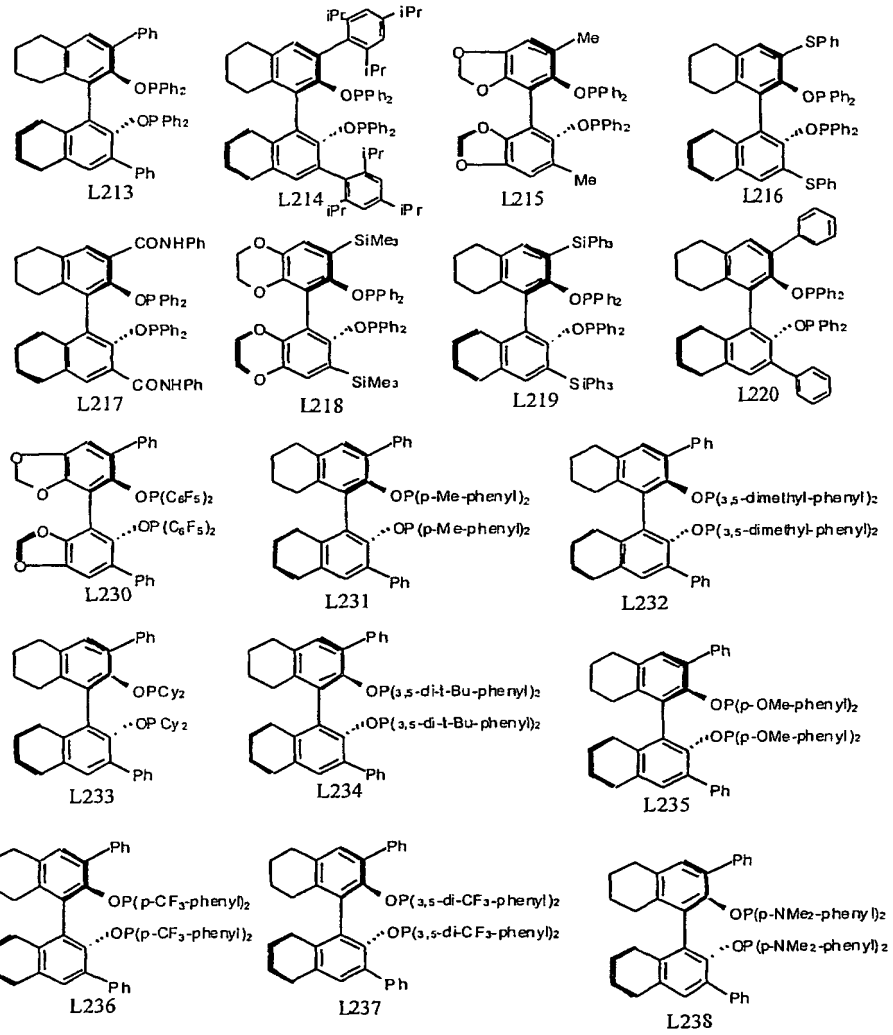

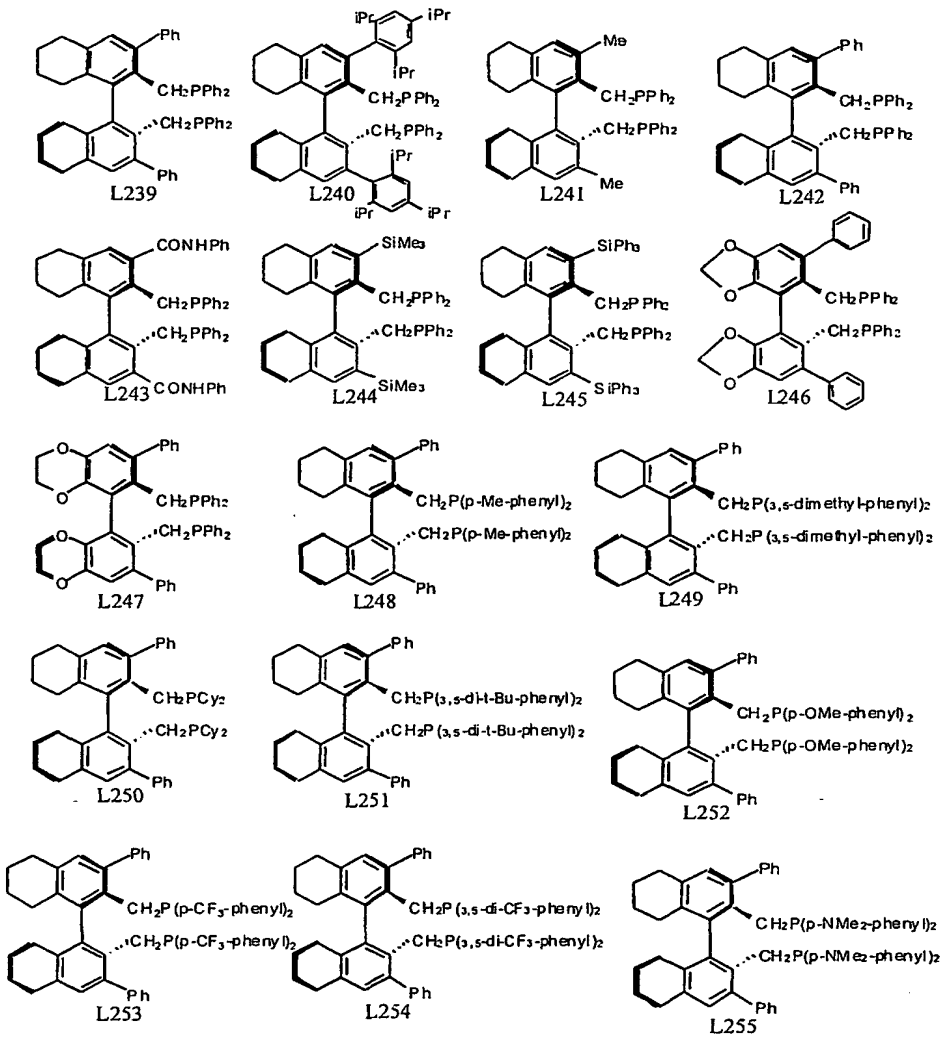

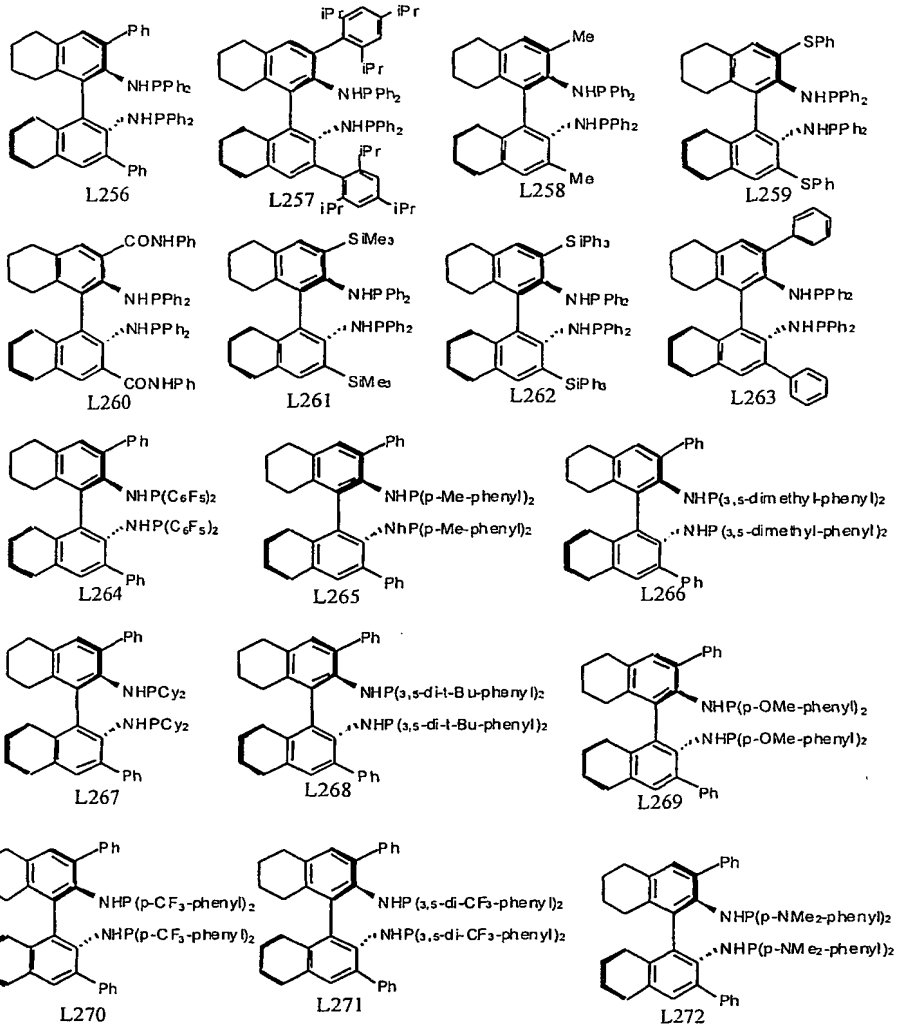

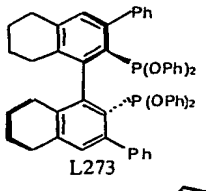
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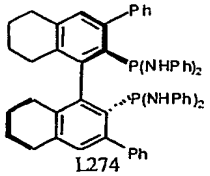
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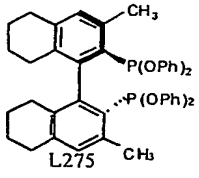
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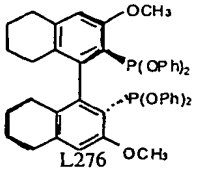
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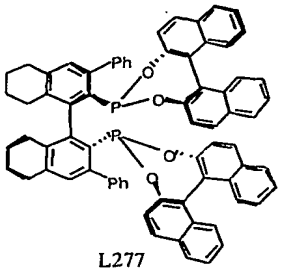
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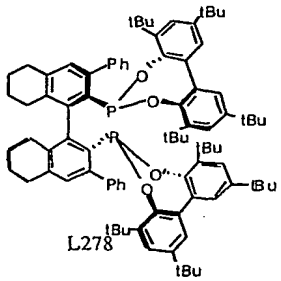
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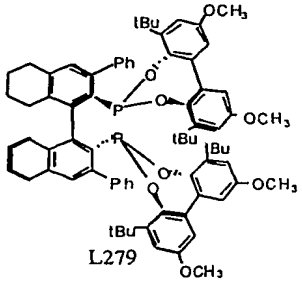
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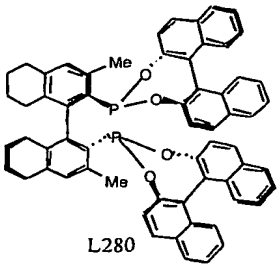
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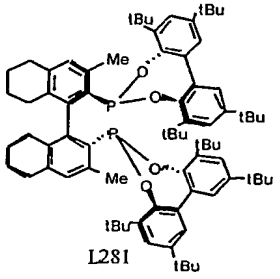
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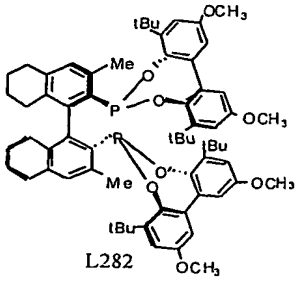
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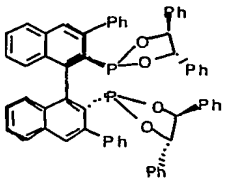
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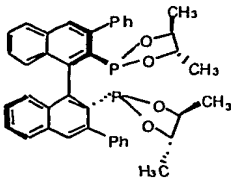
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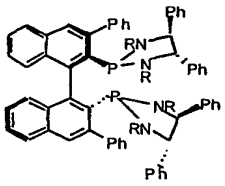
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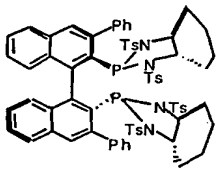
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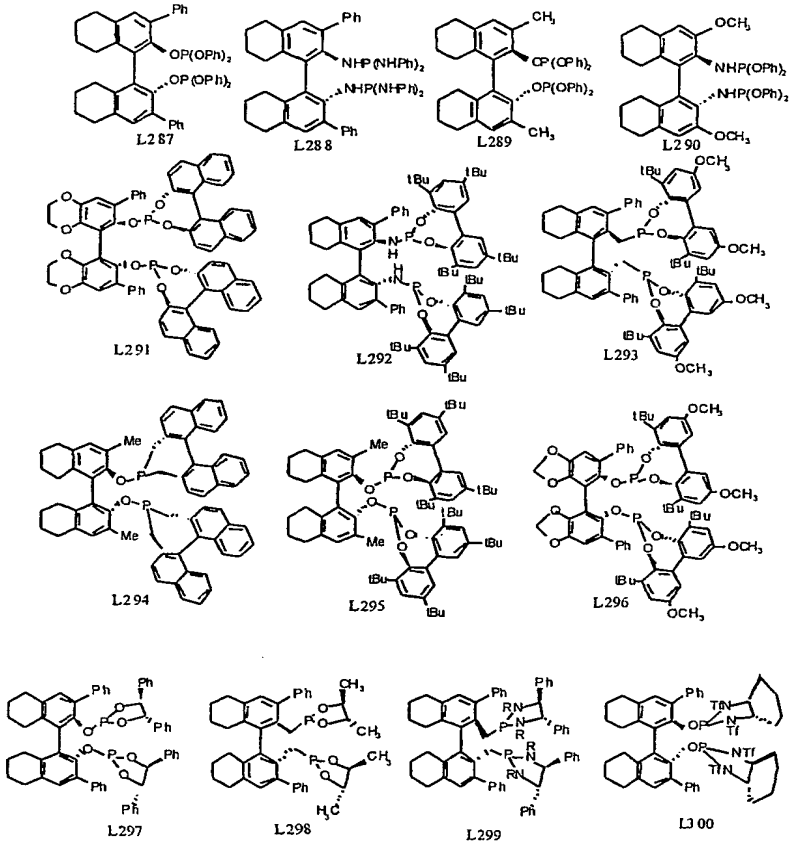

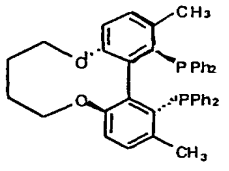
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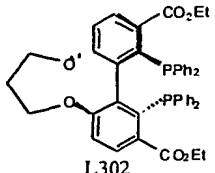
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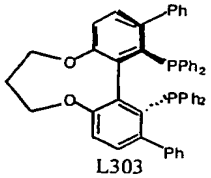
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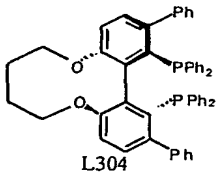
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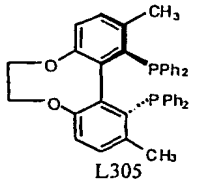
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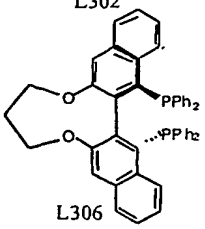
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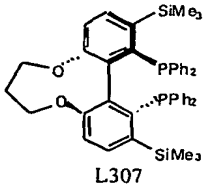
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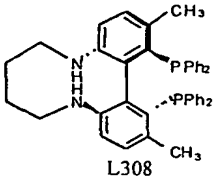
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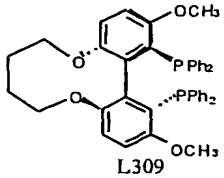
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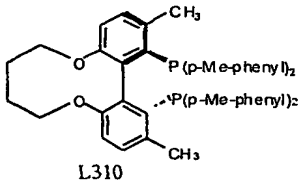
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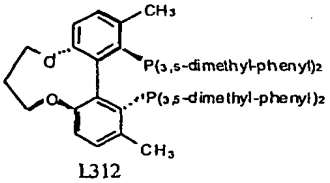
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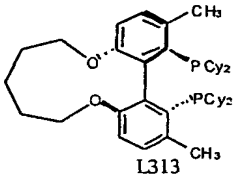
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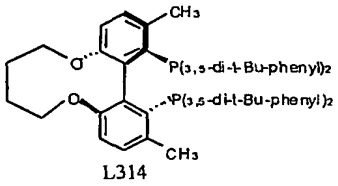
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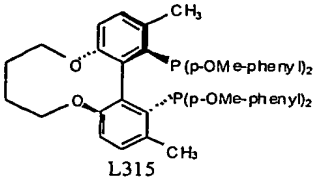
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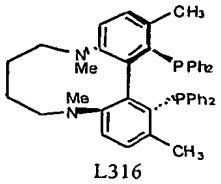
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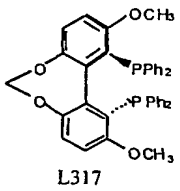
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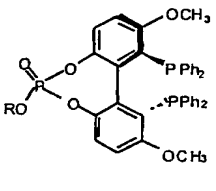
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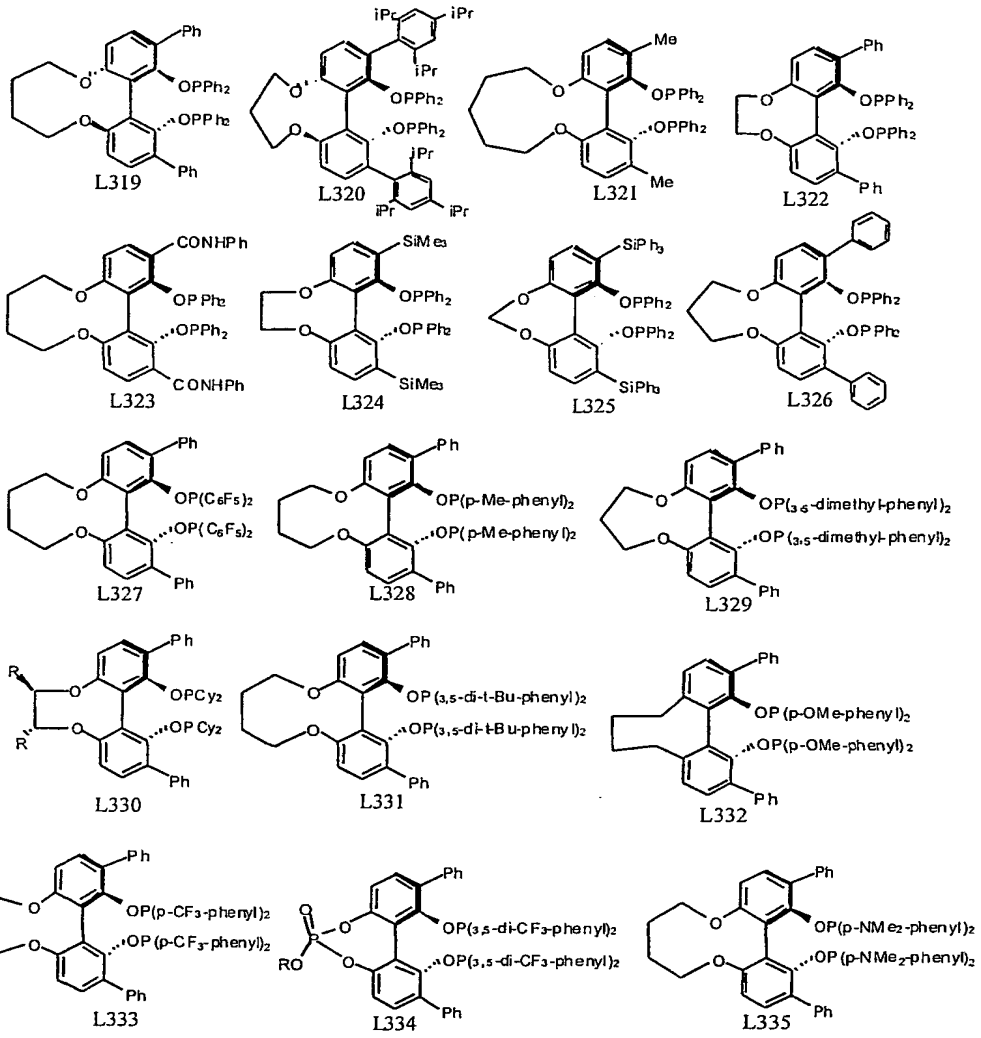
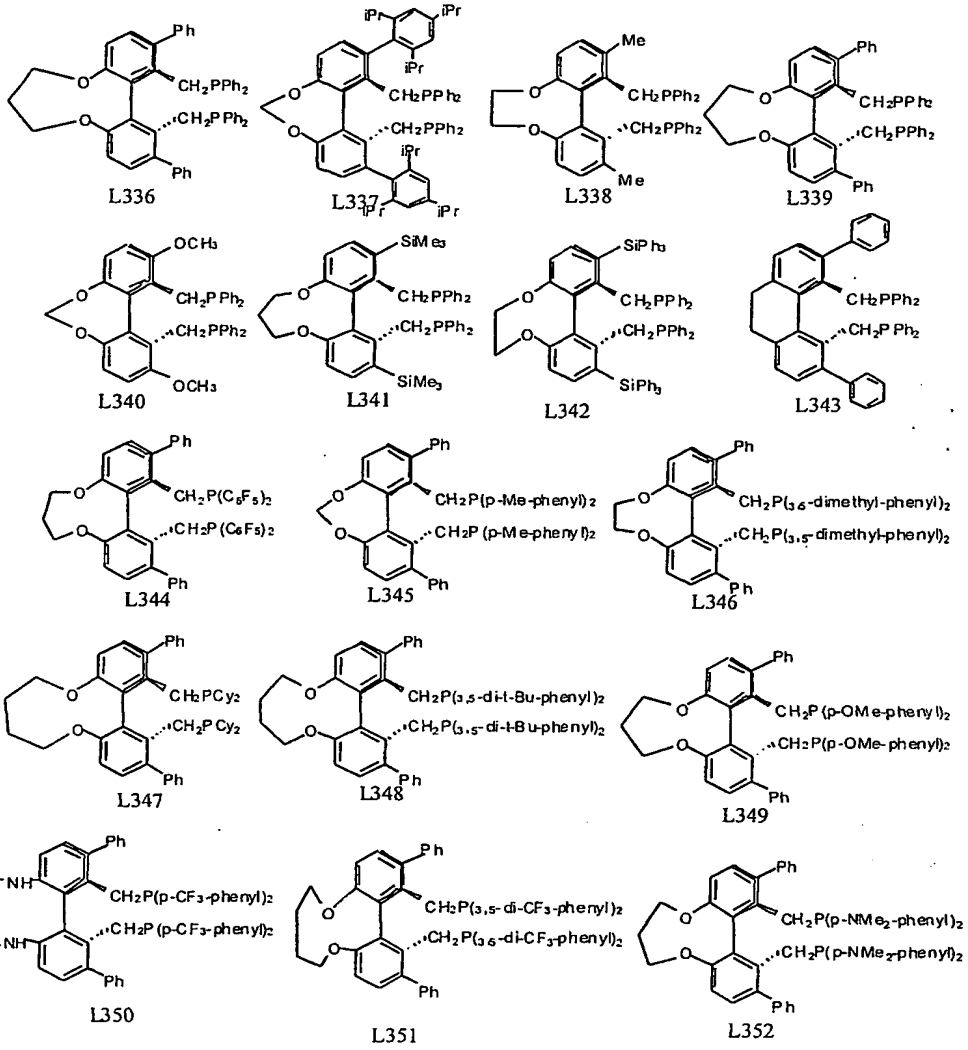
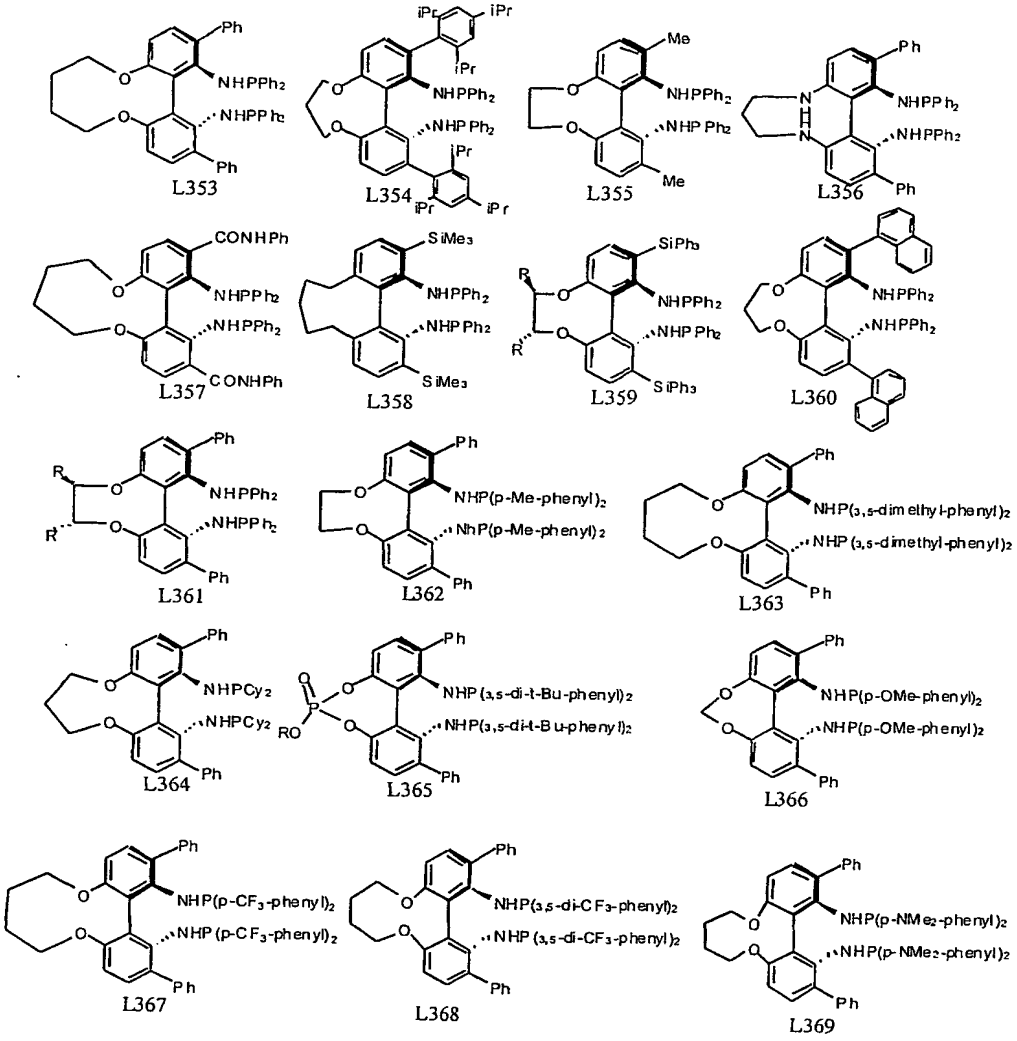
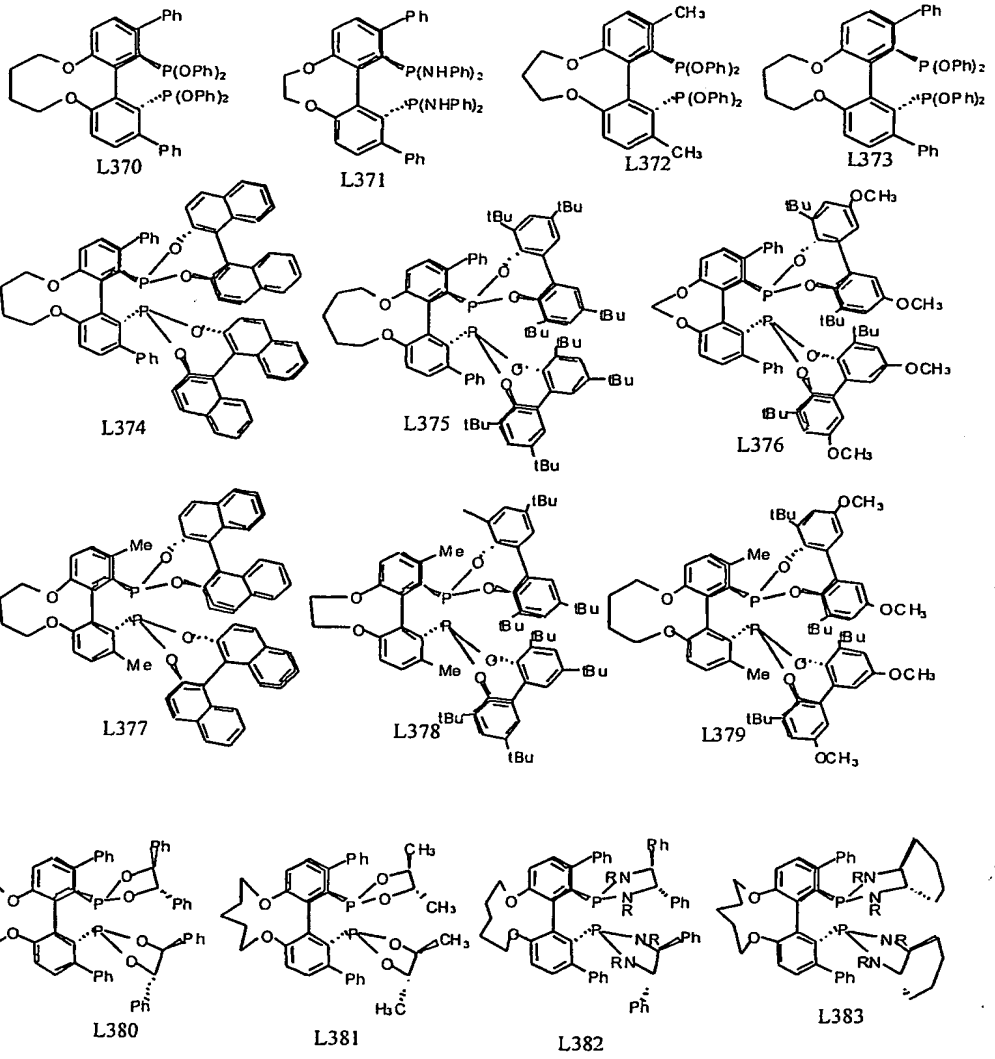
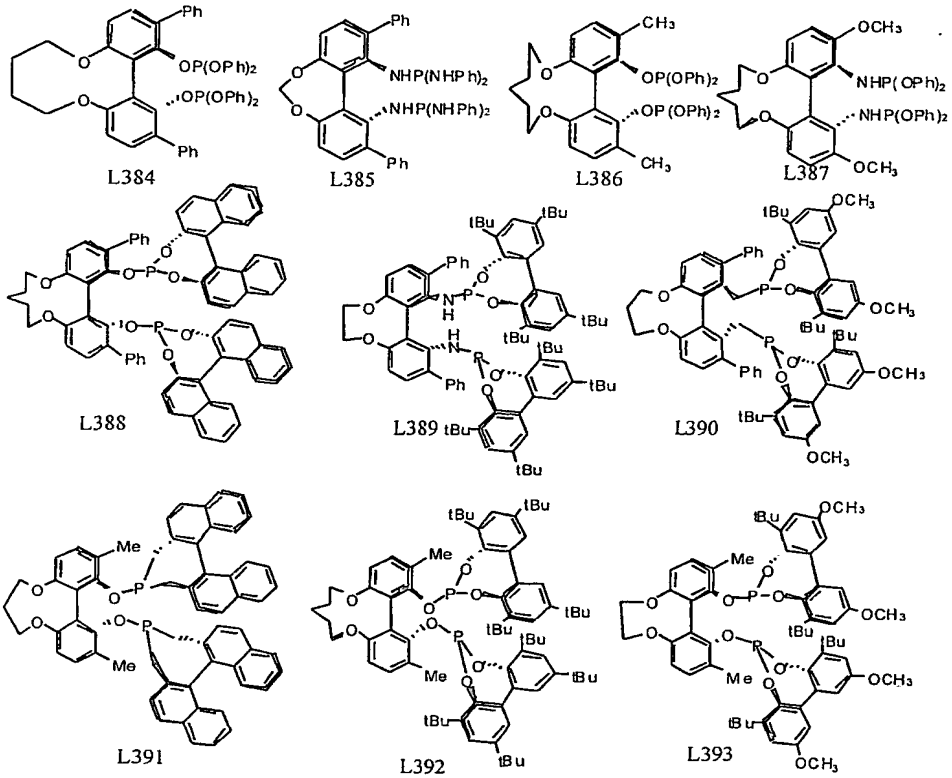










The present invention also includes a catalyst prepared by a process comprising contacting a transition metal salt, or a complex thereof, and a ligand according to the present invention. The catalyst may be prepared in situ or as an isolated compound.

The catalyst of the present invention can be a racemic mixture of enantiomers. Preferably, the catalyst is a non-racemic mixture of enantiomers, and more preferably, the catalyst is one of the enantiomers. Preferably, the catalyst has an optical purity of at least 85% ee, and more preferably, the catalyst has an optical purity of at least 95% ee.

Suitable transition metals for the preparation of the catalyst include Ag, Pt, Pd, Rh, Ru, Ir, Cu, Ni, Mo, Ti, V, Re and Mn.

As mentioned above, the catalyst can be prepared by contacting a transition metal salt or its complex and a ligand according to the present invention.

Suitable transition metal salts or complexes include the following:

AgX; Ag(OTf); $Ag(OTf)_2$; AgOAc; $PtCl_2$; H_2PtCl_4; $Pd_2(DBA)_3$; $Pd(OAc)_2$; $PdCl_2(RCN)_2$; $(Pd(allyl)Cl)_2$; $Pd(PR_3)_4$; $(Rh(NBD)_2)X$; $(Rh(NBD)Cl)_2$; $(Rh(COD)Cl)_2$; $(Rh(COD)_2)X$; Rh(acac)$(CO)_2$; Rh(ethylene)$_2$(acac); $(Rh(ethylene)_2Cl)_2$; $RhCl(PPh_3)_3$; $Rh(CO)_2Cl_2$; RuHX$(L)_2$(diphosphine), $RuX_2(L)_2$ (diphosphine), Ru(arene)X_2(diphosphine), Ru(aryl group)X_2; Ru$(RCOO)_2$(diphosphine); Ru(methallyl)2(diphosphine); Ru(aryl group)$X_2(PPh_3)_3$; Ru(COD)(COT); Ru(COD)(COT)X; RuX_2(cymen); $Ru(COD)_n$; Ru(aryl group)X_2(diphosphine); $RuCl_2$(COD); $(Ru(COD)_2)X$; RuX_2(diphosphine); $RuCl_2(=CHR)(PR'_3)_2$; $Ru(ArH)Cl_2$; Ru(COD)$(methallyl)_2$;

$(Ir(NBD)_2Cl)_2$; $(Ir(NBD)_2)X$; $(Ir(COD)_2Cl)_2$; $(Ir(COD)_2)X$; $CuX(NCCH_3)_4$; $Cu(OTf)$; $Cu(OTf)_2$; $Cu(Ar)X$; CuX; $Ni(acac)_2$; NiX_2; $(Ni(allyl)X)_2$; $Ni(COD)_2$; $MoO_2(acac)_2$; $Ti(OiPr)_4$; $VO(acac)_2$; $MeReO_3$; MnX_2 and $Mn(acac)_2$; wherein each R and R' is independently selected from the group consisting of: alkyl or aryl; Ar is an aryl group; and X is a counteranion.

In the above transition metal salts and complexes, L is a solvent and the counteranion X can be halogen, BF_4, $B(Ar)4$ wherein Ar is fluorophenyl or 3,5-di-trifluoromethyl-1-phenyl, ClO_4, SbF_6, PF_6, CF_3SO_3, RCOO or a mixture thereof.

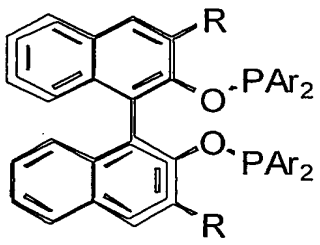
In another aspect, the present invention includes a process for preparation of an asymmetric compound using the catalysts described above. The process includes the step of contacting a substrate capable of forming an asymmetric product by an asymmetric reaction and a catalyst according to the present invention prepared by contacting a transition metal salt, or a complex thereof, and a ligand according to the present invention.

Suitable asymmetric reactions include asymmetric hydrogenation, hydride transfer, allylic alkylation, i.e., palladium-catalyzed allylic alkylation of an allylic ester, hydrosilylation, hydroboration, hydrovinylation, hydroformylation, olefin metathesis, hydrocarboxylation, isomerization, cyclopropanation, Diels-Alder reaction, Heck reaction, isomerization, Aldol reaction, Michael addition; epoxidation, kinetic resolution, i.e., palladium-catalyzed allylic alkylation of a racemic allylic ester, and [m+n] cycloaddition wherein m = 3 to 6 and n = 2, i.e., silver-catalyzed asymmetric [3 +2] cycloaddition of an azomethine ylide with a dipolarophile.

Preferably, the asymmetric reaction is hydrogenation and the substrate to be hydrogenated is an ethylenically unsaturated compound, imine, enamine, enamide, vinyl ester or a ketone, including a ketone such as a beta-ketoester.

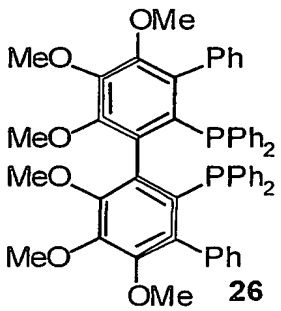
In the case of beta-ketoesters and enamides, the use of Ru as the transition metal to produce an asymmetric beta-hydroxyester and beta amino acid, respectively, is preferred, particularly when the ligand is a compound represented by one of the following formulas:

(a)



wherein each R is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl and SiR_3; and wherein each Ar is independently selected from the group consisting of: phenyl, substituted phenyl, aryl and substituted aryl;

(b)



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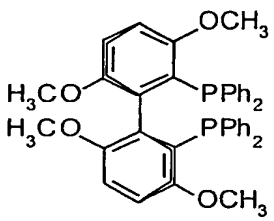
(c)



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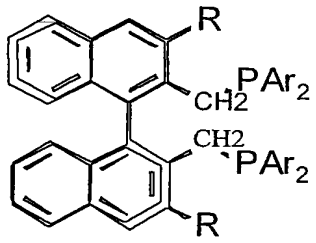
(d)



or a combination thereof.

The detailed description of ligand synthesis and asymmetric reactions thereof is provided below.

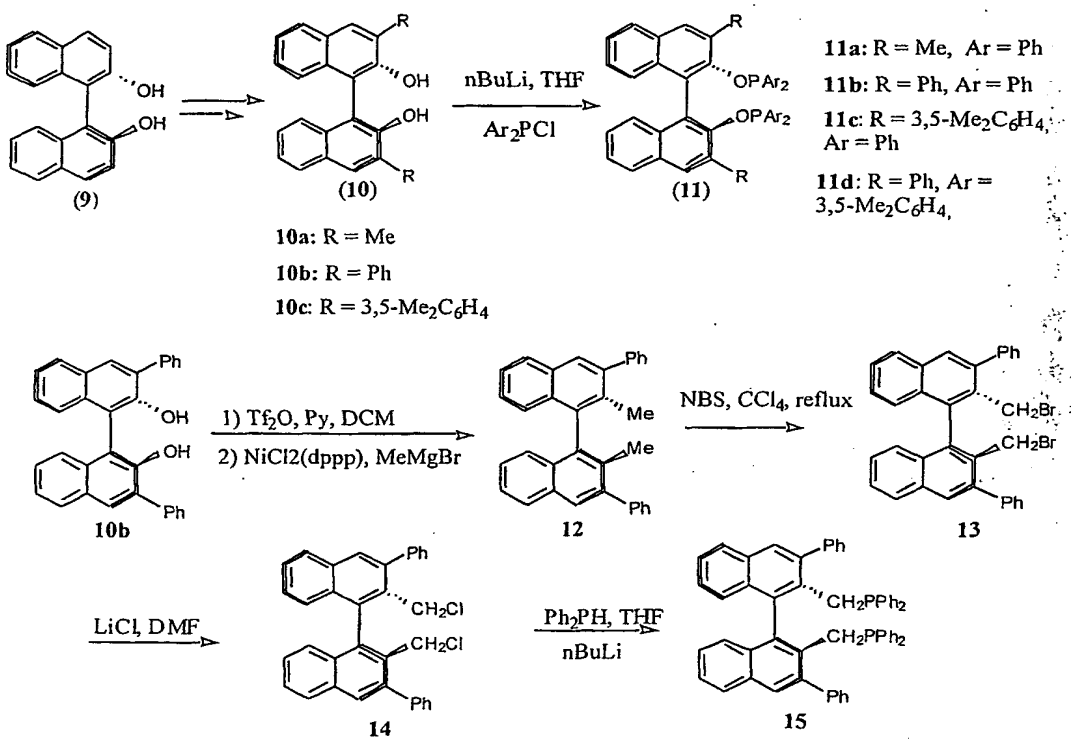
General procedures

All reactions and manipulations were performed in a nitrogen-filled glove box or using standard Schlenk techniques. THF and toluene were dried and distilled from sodium-benzophenone ketyl under nitrogen. Methylene chloride was distilled from CaH_2. Methanol was distilled from Mg under nitrogen. (R, R)-BDNPB was made a solution of 10mg/ml in toluene before use. Column chromatography was performed using EM silica gel 60 (230~400 mesh). ^{1}H, ^{13}C and ^{31}P NMR were recorded on Bruker WP-200, AM-300, and AMX-360 spectrometers. Chemical shifts were reported in ppm down field from tetramethylsilane with the solvent resonance as the internal standard. Optical rotation was obtained on a Perkin-Elmer 241 polarimeter. MS spectra were recorded on a KRATOS mass spectrometer MS 9/50 for LR-EI and HR-EI. GC analysis was carried on Helwett-Packard 6890 gas chromatography using chiral capillary columns. HPLC analysis was carried on Waters™ 600 chromatography.

Ligand Synthesis

Ligand Synthesis

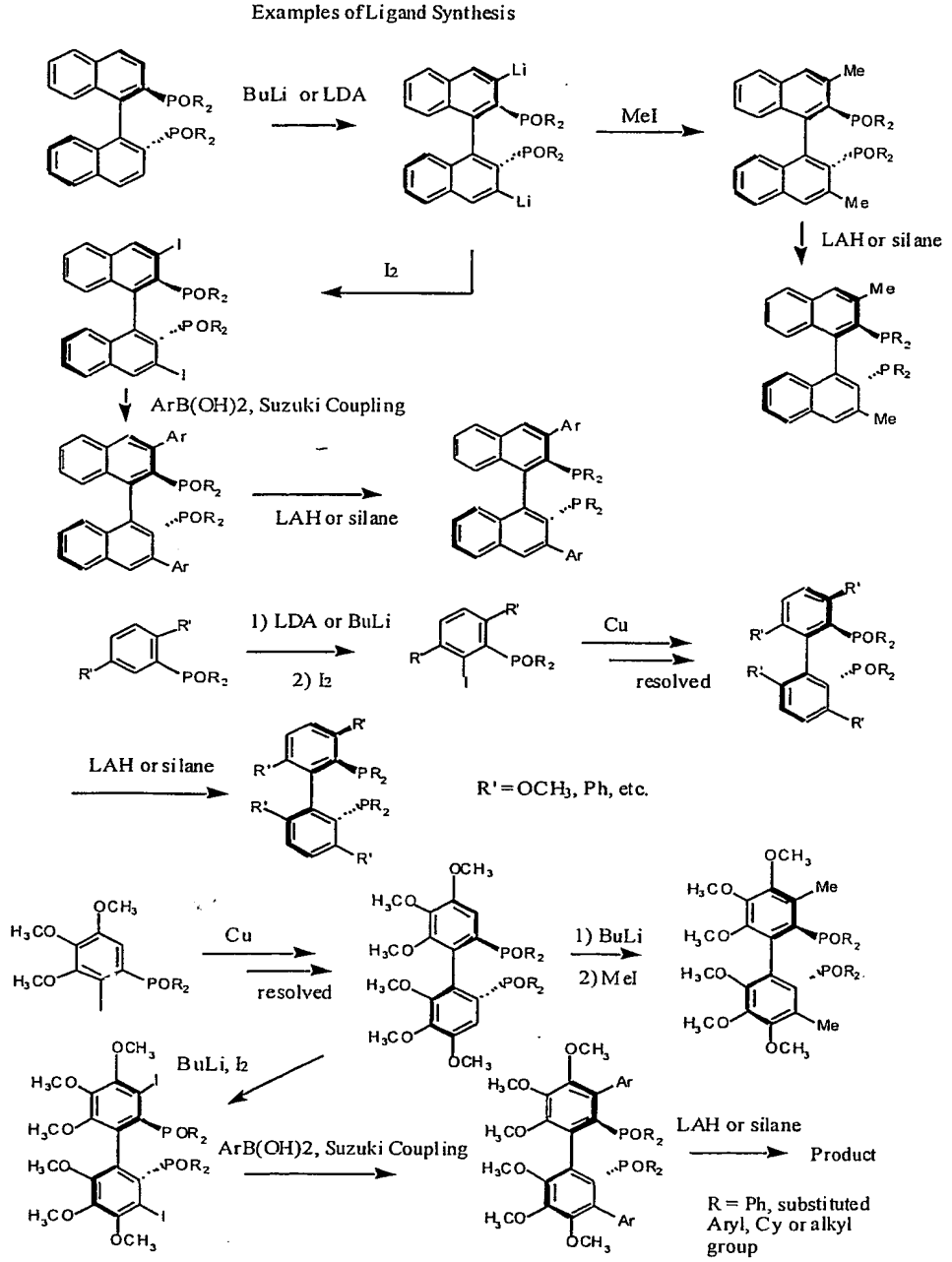
Several chiral ligands have been prepared and used for asymmetric hydrogenation reactions. Scheme 1 shows the synthesis of these ligands. The starting material, enantiomerically pure BINOL can be converted to many chiral phosphines and phosphinites (**11a-L20, 11b-L18, 11c-L31, 11d** and **15-L38**). 3,3'-disubstituted BINOL was prepared from (*S*)-BINOL according to known literature methods (Cox, P. J. et al. *Tetrahedron Lett.* **1992**, *33*, 2253; Simonsen, K. B. et al. *J. Org. Chem.* **1998**, *63*, 7536).



Scheme 1. Ligand Synthesis

Chiral bisphosphinite ligands (**11a-L20, 11b-L18, 11c-L31, 11d**) were made through reaction of chlorodiaryl phosphine with the corresponding chiral diols (**10a-10c**) in high yields. Chiral bisphosphine **15** was made from 3,3'-diphenyl-2,3'dihydroxyl-1,1'- binaphthyl (**10b**) in a few steps. Compounds **12-14**

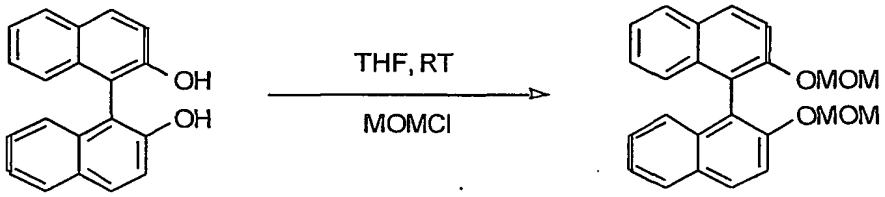
were synthesized according to a reported procedure (Xiao, D. et al. *Org. Lett.* **1999**, *1*, 1679). Representative examples can be synthesized by a variety of methods. Several such methods suitable for use in the synthesis of chiral 3,3'disubstituted bisaryl phosphines, are described below:



EXAMPLE 1

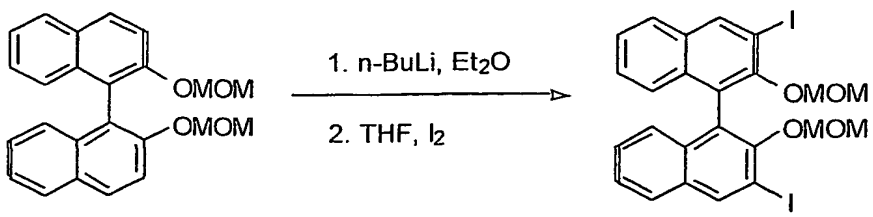
Synthesis of a 3,3'-Disubstituted Chiral BINOL (10b)

(R)-2,2'-Bismethoxymethoxy-1,1'-binaphthyl



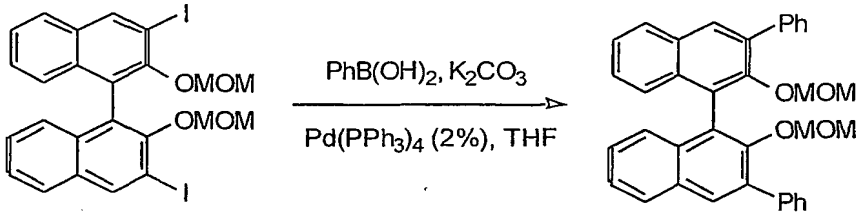
To a THF (200 ml) solution of NaH (5.52 g, 230 mmol) was added (R)-BINOL (28.6g, 100 mmol) solution in THF (50 ml) under nitrogen at zero temperature, after 30 min, chloromethyl methyl ether (17.09 ml, 225 mmol) in 30 ml THF was added dropwise. The mixture was stirred overnight at room temperature. 3 ml water was added carefully to destroy the excess NaH, and filtered to remove the inorganic salt. The solution was passed a silica gel plug (hexane/ethyl acetate = 1/1) to give pure product (97% yield).

(R)-3,3'-diiodo-2,2'-Bismethoxymethoxy-1,1'-binaphthyl

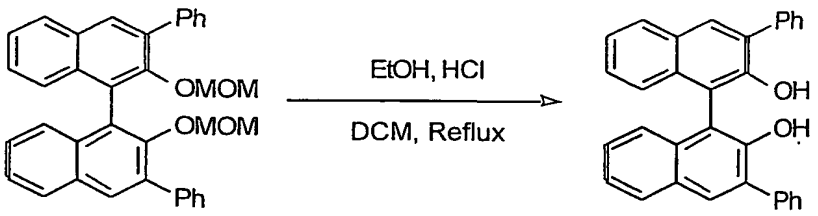


To a solution of (R)-2,2'-Bismethoxymethoxy-1,1'-binaphthyl (37.4g, 100mmol) in diethyl ether (400 ml) was added *n*-BuLi (100 ml, 2.5 M in hexane, 250 mmol) at room temperature under nitrogen, the mixture was stirred for 3 hours, then was cooled to 0°C, 200 ml THF was added, after 10 min, a solution of iodine (300 mol, 76.2g) in THF (60 ml) was added dropwise. The mixture was allowed to warm to room temperature over 4 hours. 100 ml saturated Na_2SO_3 aqueous was added to destroy the excess iodine, then extracted with ethyl acetate, organic phase was washed with 100 ml saturated Na_2SO_3, 3X100 ml water, dried over sodium sulfate and evaporated. The residue was purified by a silica gel column eluted with (hexane /ethyl acetate = 7/1) to give product as a yellow solid (80% yield, contain 5-7% monoiodo-substituted product).

(R)-3,3'-diphenyl-2,2'-Bismethoxymethoxy-1,1'-binaphthyl



To a solution of (R)-3,3'-diiodo-2,2'-Bismethoxymethoxy-1,1'-binaphthyl (90 mmol, 56.3g) and phenylboronic acid (25.2 g, 225 mmol) in THF 800 ml, was added $Pd(PPh_3)_4$ (2.3 g, 2 mmol) and degassed 1M K_2CO_3 aqueous solution (400 ml, 400 mmol). The reaction mixture was heated at reflux for 20 hours. The mixture was extracted with ethyl acetate, and combined organic layer was washed with brine. Evaporation of the solvent gave a yellow solid (47g). The residue was used to next step without other purification.



(R)-3,3'-diphenyl-1,1'-binaphthol

To a solution of (R)-3,3'-diphenyl-2,2'-Bismethoxymethoxy-1,1'binaphthyl (47 g) in a mixture solvent of 200 ml DCM and 500 ml EtOH was added concentrated HCl (90 ml). The reaction mixture was heated at reflux under nitrogen for 16 hours. The volatile components were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (DCM/hexanes=4/6) to give the product (25.2 g, 57.6 mmol, 64% yield for two steps)

EXAMPLE 2

Alternative Route for the Synthesis of a 3,3'-Disubstituted Chiral BINOL (10b)

(S)-2,2'-Dimethoxy-1,1'-dinaphthyl

To a solution of (S)-2,2'-dihydroxy-1,1'-dinaphthyl (100g, 349.7 mmol) in 1000ml 95% EtOH was added dimethyl sulfate (93.1ml, 981.7 mmol, 2.8eq.) and followed by dropwise addition of a solution of NaOH (175g) in 300ml H_2O. After the addition, the resulting system was heated to reflux for 3 h, and then cooled. The reaction mixture was filtered, the precipitate was collected and

washed with 10% aqueous NaOH (3×150 ml), and recrystallized from toluene (reflux to dissolve into 700 ml toluene, then let it stay at 0 °C overnight) to yield 84.1g white crystal product (S)-2,2'-dimethoxy-1,1'-dinaphthyl (yield = 76.6%). ^{1}H-NMR ($CDCl_3$):δ7.985(d, *J*=9.0Hz, 2H, Ar-H), 7.875(d, *J*=8.1Hz, 2H, Ar-H), 7.468(d, *J*=9.0Hz, 2H, Ar-H), 7.300~7.326(t, 2H, Ar-H), 7.199~7.218(t, 2H, Ar-H), 7.118(d, *J*=8.1Hz, 2H, Ar-H), 3.773(s, 6H, -OCH_3).

(*S*)-3,3'-Bis(dihydroxyborane)-2,2'-Dimethoxy-1,1'-dinaphthyl

Under N_2, in a 500 ml Schlenk flask were placed 300 ml of dry *t*-butyl-methyl ether and TMEDA (14.4 ml, 95.5 mmol, 3equiv). To this solution was added 2.5M *n*-BuLi in hexane(39.5 ml, 98.7 mmol, 3.1 equiv), the resulting solution was stirred for 30 min. at room temperature, solid (S)-2,2'-dimethoxy-1,1'-dinaphthyl (10g, 31.8mmol) was added in one portion under N_2 flow, the reaction system was stirred at room temperature for 3hrs.The resulting brown slurry was cooled to -78°C, and $B(OEt)_3$ (33.9 ml, 197.5 mmol, 6.2equiv) was dropwise introduced over a period of 15min. The reaction system was allowed to warm room temperature and was left stirring overnight. The reaction was quenched with 150ml aqueous 1M HCl solution, and was stirred for another 2 h. The phase was separated, the organic phase was washed with aqueous 1M HCl solution (3 × 100mL) and saturated aqueous NaCl solution (3 × 100 ml), and dried over Na_2SO_4. The solvent was removed, and the resulting white solid were recrystallized twice from 70ml toluene (reflux to dissolve into 700ml toluene, then let it stay at 0 °C overnight, and recrystallization once can't remove by-product completely) to give the product (*S*)-3,3'-Bis(dihydroxyborane)-2,2'-Dimethoxy-1,1'-dinaphthyl 9.33g (Yield = 73.3%).^{1}H-NMR(Acetone-d_6):δ 8.556(s, 2H, Ar-H), 8.041(d, *J*=8.1Hz, 2H, Ar-H), 7.454(t, 2H, Ar-H), 7.335(t, 2H, Ar-H), 7.112(d, *J*=8.1Hz, 2H, Ar-H), 3.773(s, 6H, -OCH_3). ^{1}H-NMR shows that toluene is very difficult to remove completely, but there is no any influence on the secondary reaction.

(*S*)-3,3'-Diphenyl-2,2'-dimethoxy-1,1'-dinaphthyl

In a 50ml Schlenk flask were placed (*S*)-3,3'-bis(dihydroxyborane)-2,2'-dimethoxy-1,1'-dinaphthyl(1.206 g, 3 mmol), $Ba(OH)_2.8H_2O$ (2.739g, 8.7mmol, 2.9 equiv), and $Pd(PPh_3)_4$ (183 mg, 0.15 mmol, 5% mol), the reaction system was evacuated and filled with N_2 for three times, 1,4-dioxane(18ml), H_2O(8ml), and bromobenzen(1.89ml,18mmol, 6eq.) were added. The reaction system was heated under reflux for 24 hrs under N_2 and cooled to room temperature. The 1,4-dioxane was removed, and the resulting mixture was redissolved into 100ml CH_2Cl_2, and washed with aqueous 1M HCl solution (3× 50 ml) and saturated aqueous NaCl solution(2 × 50 ml), and dried over Na_2SO_4. The solvent was removed to yield crude product (*S*)-3,3'-diphenyl-2,2'-dimethoxy-1,1'-dinaphthyl 1.513 g as orange syrup.

This intermediate was not isolated and was used directly in the final step.

(S)-3,3'-Diphenyl-2,2'-dihydroxy-1,1'-dinaphthyl (10b)

The crude product diphenyl-2,2'-dimethoxy-1,1'-dinaphthyl (1.513g, approximately 3mmol) was dissolved into 80 ml dry CH_2Cl_2, and cooled to -78°C, BBr_3(1.5 ml) was added in 10 min., and the reaction system was stirred for 18 h at room temperature. The resulting slight brown solution was cooled to 0°C, and 200 ml H_2O was added carefully. The phase was separated, and the organic phase was washed with H_2O (5 × 80 ml) and saturated aqueous NaCl solution (2 × 50 ml), and dried over Na_2SO_4. The solvent was removed, and the resulting solid was recrystallized from 10 ml MeOH to yield ***(S)*-10b** as white-gray powder (overall yield of coupling and deprotection steps, 61.8%).

^{1}H-NMR($CDCl_3$):δ8.029(s, 2H, Ar-H), 7.929(d, J = 7.9Hz, 2H, Ar-H), 7.741(dd, 4H, J = 7.9 1.4Hz Ar-H), 7.499(t, 4H, Ar-H), 7.376~7.434 (m, 4H, Ar-H), 7.325 (td, 2H, J = 7.9 1.3Hz Ar-H), 7.250(t, 2H, Ar-H), 5.364(br, 2H, -OH).

EXAMPLE 3

Synthesis of a 3,3'-Disubstituted Chiral Phosphinite, (R)-3,3'-diphenyl-2,2'-bisdiphenylphosphinooxy-1,1'-binaphthyl (11b)

To a solution of (*R*)-3,3'-diphenyl-1,1'-binaphthol (876 mg, 2 mmol) in 20 ml THF at -78°C was added *n*-BuLi (2.8 ml, 4.5 mmol) dropwise, the mixture was warmed to room temperature and stirred for 30 min, then cooled to -78°C, Ph_2PCl (0.9 ml, 5 mmol) was added *via* syringe, then warmed to room temperature and stirred overnight. The THF was removed under reduced pressure, the residue was purified by basic Al_2O_3 (EtOAc/Hexane/Et_3N = 90/8/2) to give pure product (1.41 g, 87% yield).

^{1}H-NMR (CD_2Cl_2, 360 MHz) 6.80-7.20 (m, 24H), 7.35-7.48 (m, 12H), 7.50-7.65 (m, 4H).). ^{31}P-NMR (CD_2Cl_2, 360 MHz) 112.78.). ^{13}C-NMR (CD_2Cl_2, 360 MHz) 124-150 (m). $[\alpha]_D^{20}$=114.7 (c, 0.38, $CHCl_3$). MS: 203 (100), 387 (65), 439 (48), 807 (50). HRMS $C_{56}H_{41}O_2P_2$ 807.2566 Cal.: 807.2582.

EXAMPLE 4

General Procedure for Catalytic Asymmetric Hydrogenation of Enamides

In a glove box, the Rh-phosphine complex was made *in situ* by mixing $Rh(COD)_2PF_6$ (3.7 mg, 0.008 mmol) and a chiral phosphine ligand (0.8 ml of 10mg/mL ligand in toluene, 0.012 mmol) in 19.2 ml of CH_2Cl_2. The mixture was

stirred for 30 min. Then 2.5 ml of this solution was transferred to a 10 ml vial with an enamide substrate (0.1 mmol).

The hydrogenation was performed at room temperature under 20 psi of hydrogen pressure for 24 h. The hydrogen was released carefully and the reaction mixture was passed through a silica gel plug eluted with EtOAc. The enantiomeric excess was measured by GC or HPLC using a chiral GC or HPLC column without further purification. The absolute configuration of products was determined by comparing the sign of optical rotation with the reported data.

EXAMPLE 5

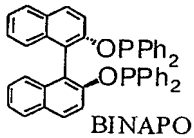
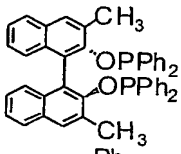
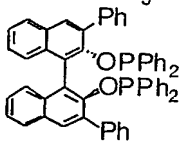
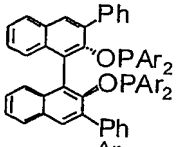
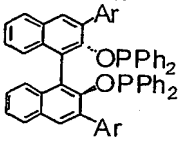
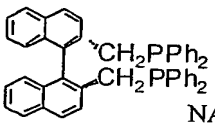
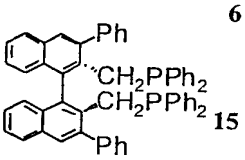
Results of Asymmetric Hydrogenation of Enamides

To examine the effectiveness of new chiral ligands, hydrogenation of a typical dehydroamino acid derivative and an enamide was carried out. The results are summarized in Table 1. The 3,3'disubstituted bisphosphinite ligands (**11a-d**) are more effective than BINAPO (**3**) for asymmetric hydrogenation.

In the similar way, the 3,3'-disubstituted bisphosphine **15** is a better ligand for Rh-catalyzed asymmetric hydrogenation than NAPHOS (**6**).

We conclude that introduction of 3,3' substituted groups can restrict the rotation of phenyl groups adjacent to phosphines and therefore a well-defined chiral pocket around the transition metal is formed. The conformational rigidity is crucial for achieving high enantioselectivity for a number of asymmetric reactions.

Table 1. Rh(I) -catalyzed asymmetric hydrogenation

Ligand	Substrate: NHAc / COOMe	Substrate: NHAc / Ph
entry 1  BINAPO **3**	73% ee	28%ee
entry 2  **11a**	95 %ee	67% ee
entry 3  **11b**	>99 % ee	94% ee
entry 4  **11c**	95% ee	89% ee
entry 5  **11d**	93%ee	90% ee
entry 6  NAPHOS **6**	54% ee	—
entry 7  **15**	99% ee	82% ee

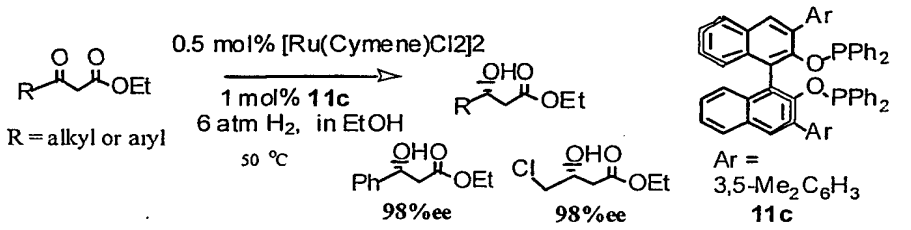
The reaction was carried out at rt under 3atm of H2 for 12 h in 3ml of THF with complete conversion (S/C = 100). Ar = 3,5-$Me_2C_6H_4$

EXAMPLE 6

Asymmetric Hydrogenation of Beta-keto Esters

A number of beta-ketoesters can be reduced in high ee's using a Ru-3,3'substituted BINAPO (**11d**) compound as the catalysts. Particularly, the R group is aryl, hetereoaryl, substituted aryl, alkyl and substituted alkyl species. These reactions can be carried out at low pressure and low temperature, which shows advantages over the reaction carried out with Ru-BINAP complex (90 atm, 90 °C).

Asymmetric Hydrogenation



EXAMPLE 7

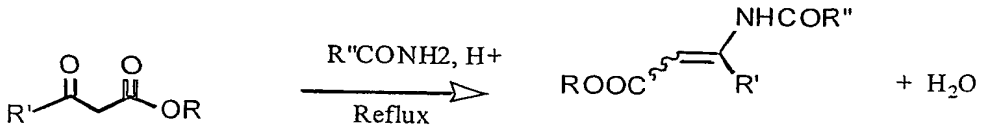
Asymmetric Synthesis of Beta-Amino Acids

Synthesis of Starting Material 3-Acetamido-3-Aryl-2-Propenoates and 3-Acetamido-3-hetero-Aryl-2-Propenoates

Typical procedure: The starting material methyl 3-acetamido-3-phenyl-2-propenoate can be conveniently synthesized from cheap acetophenone in three steps according to known literature procedure in good yields. The literatures are Zhu, G.; Zhen, Z.; Zhang, X. *J. Org. Chem.* **1999**, *64*, 6907-6910; Krapcho, A. P.; Diamanti, J. *Org. Synth.* **1973**, *5*, 198-201. ^{1}H-NMR ($CDCl_3$, 360 MHz) δ (Z

isomer) 2.17 (s, 3H), 3.77 (s, 3H), 5.29 (s, 1H), 7.37-7.45 (m, 5H); (E isomer) 2.38 (s, 3H), 3.77 (s, 3H), 6.65 (s, 1H), 7.37-7.45 (m, 5H).

An Effective New Way to Make Enamides



E/Z mixture

R', R" = alkyl, substituted alkyl, aryl, substituted aryl, hetereoaryl

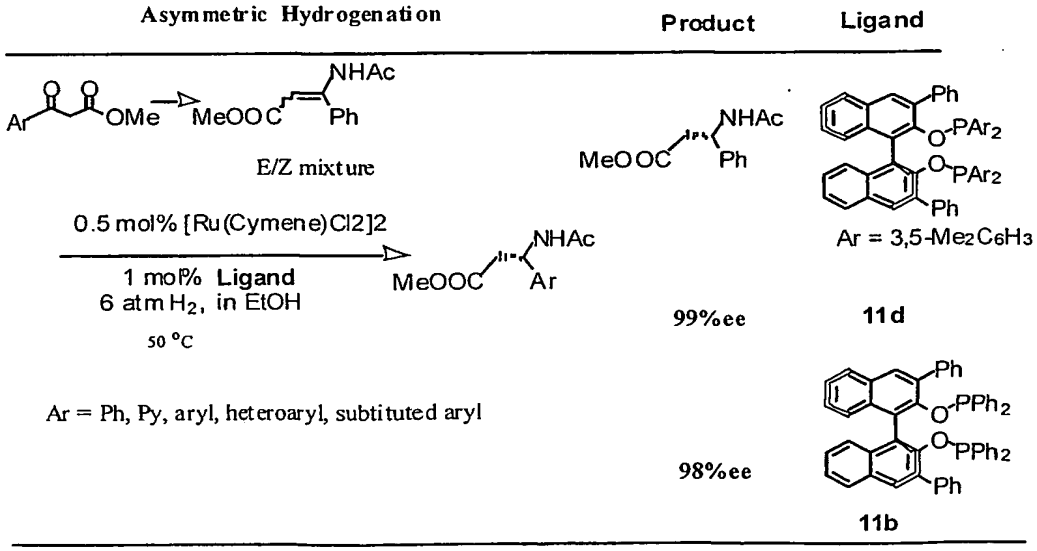
R = alkyl, aryl

Alternatively, 3-acetamido-3-aryl-2-propenoates and 3-Acetamido-3-hetero-aryl-2-propenoates can be prepared through a new route by reacting acetamide with the corresponding beta-keto esters. A related example is demonstrated by Tschaen et al. *J. Org. Chem.* 1995, 60, 4324. The typical procedure involves addition of the corresponding beta keto-ester, an acetamide or other amide such as enamide, Amberlyst 15 or other acid catalysts in toluene. The mixture was heated at reflux for some hours with removal of water using a Dean-Stark trap. The end product was obtained after evaporating the solvent.

Asymmetric Hydrogenation of methyl 3-acetamido-3-phenyl-2-propenoate

A dry Schlenk tube is charged with $[Ru(cymene)Cl_2]_2$ (1.53 mg, FW = 612, 0.0025 mmol), chiral ligand 3,3'-diphenyl-xylyl BINAPO (11d, 4.82 mg, FW = 918, 0.0053 mmol), and then is evacuated and filled with argon. DMF (must be degassed by freeze-thaw cycles) (1 ml) is introduced under stream of argon. The solution is stirred at 100 °C for 10 min under argon, giving a clear reddish brown solution. The reaction mixture is cooled and concentrated at 1 mmHg at 50 °C with vigorous stirring and then at 0.1 mmHg for 1 h to give a reddish brown solid, which is used as hydrogenation catalyst.

To a solution of above catalyst in EtOH/DCM (4 ml, 3/1) in a glove box was added substrate methyl 3-acetamido-3-phenyl-2-propenoate (109 mg, 0.5 mmol). The hydrogenation was performed at 50 °C under 78 psi of hydrogen for 15 hours (not be optimized). The bomb was then cooled to room temperature and hydrogen carefully released. The solvent was removed and the residue dissolved in ether. The ether solution was washed with water and brine and dried over sodium sulfate. The ether solution was passed through a short silica gel column and concentrated to dryness to give pure products methyl 3-acetamido-3-phenyl-2-propanoate (known compound, see: Zhu, G.; Zhen, Z.; Zhang, X. *J. Org. Chem.* **1999**, *64*, 6907-6910 (Rh/Duphos and BICP, 65% ee); Lubell, W. D.; Kitamura, M.; Noyori, R. *Tetrahedron: Asymmetry* **1991**, *2*, 543 (Ru/BINAP, poor ee)). ^{1}H-NMR ($CDCl_3$, 360 MHz) δ 1.92 (s, 3H), 2.76-2.83 (m, 2H), 3.53 (s, 3H), 5.34 (m, 1H), 6.65 (br, 1H), 7.18-7.27 (m, 5H). Chiral GC Condition: Chiral Select-1000 column (dimensions 15m X 0.25 mm (i.d.)). Carrier gas: He (1 ml/min), 180 °C, isothermal; (S) t_1 = 11.68 min; (R) t_2 = 12.04 min.

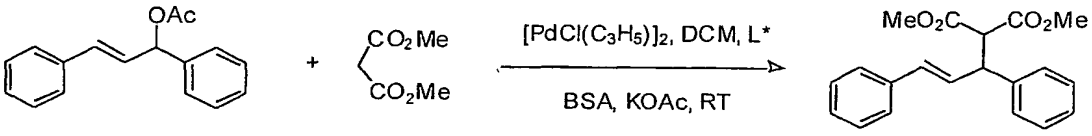


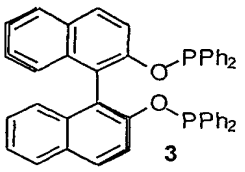
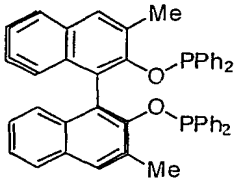
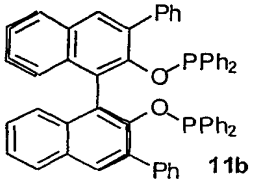
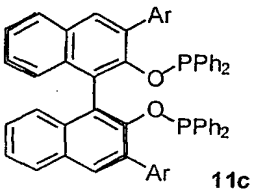
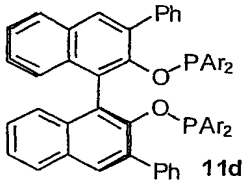
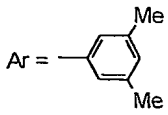
EXAMPLE 8

Asymmetric Allylic Alkylation

Using 3,3'disubstituted BINAPO as ligands, the Pd-catalyzed asymmetric allylic alkylation can be carried out and some results are listed below:

Pd-Catalyzed asymmetric allylic substitution



Ligand	ee	Ligand	ee
 **3**	69% ee	 **11a**	73%ee
 **11b**	84% ee	 **11c**	77% ee
 **11d**	95% ee	Ar = 	

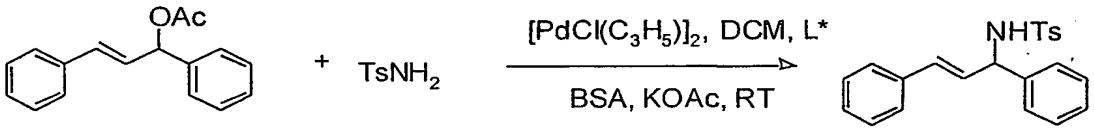
Ee values are determined by chiral HPLC (OJ Column H/IPA = 95/5)

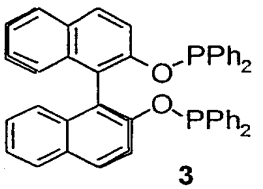
EXAMPLE 9

Asymmetric Allylic Alkylation with nitrogen nucleophile

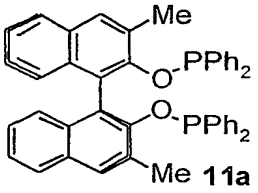
Using 3,3'disubstituted BINAPO as ligands, Pd-catalyzed asymmetric allylic alkylation with nitrogen nucleophiles can be carried out and some results are listed below:

Pd-Catalyzed asymmetric allylic substitution

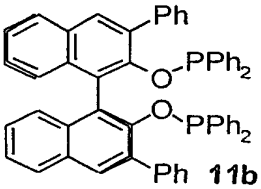




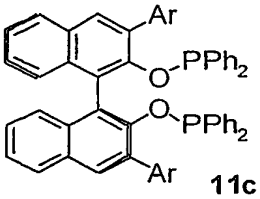
3 41% ee



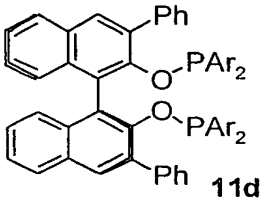
11a 63% ee



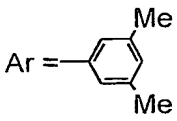
11b 94%ee



11c 76% ee



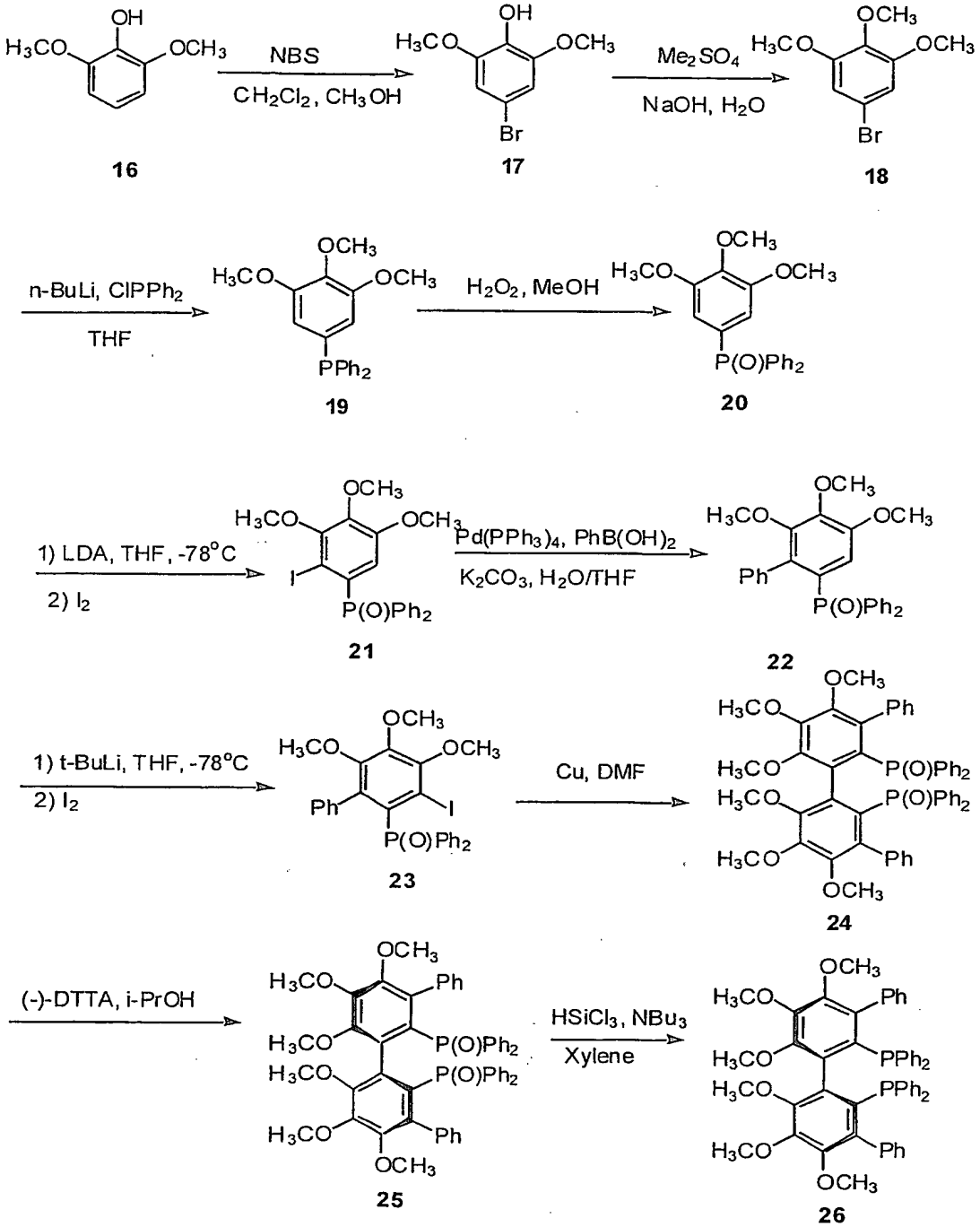
11d 90% ee



Ee values are determined by chiral HPLC (OJ Column H/IPA = 85/15)

EXAMPLE 10

Synthesis of 3,3'-disubstituted biaryl phosphines(-)-(3,3'-diphenyl-4,4',5,5',6,6'-hexamethoxybiphenyl-2,2'diyl)bis(diphenylphosphine)



Synthesis of 4-bromo-2, 6-dimethoxy-phenol 17

To a 2 liter flask equipped with a magnetic stirrer, thermometer, and nitrogen inlet, was added 77g (0.5 mol) of pyrogallol 1, 3-dimethyl ether, 5.8 ml of MeOH, and 750ml of CH_2Cl_2. To this solution was added 126mg (5mmol) of NaH (95%). The solution was stirred while cooling to –45°C with a dry-ice acetone bath. 94g (0.53mol) of powdered N-bromosuccinimide was added rapidly. The reaction mixture was then stirred for 1hour at –35°C, heated to room temperature over next 30min, and finally refluxed for 30min. The CH_2Cl_2 was removed under reduced pressure and the residue solidified. The tan solid was broken up and stirred well with 1 liter of ether. This was filtered and the residue was washed well with ether. The ether was evaporated under reduced pressure to yield a tan solid. The solid was placed in a 5 liter flask with 3 liters of ligroin (bp: 90-110°C) and heated with stirring to 80°C. The hot solution was decanted from the brown oil and the hot yellow solution was allowed to cool at room temperature for 3hr. The white needles was filtered off and dried to yield 74g (63%) of **17**.

Ref: *J. Org. Chem.* Vol. 50, **1985**, 1099.

Synthesis of 3,4, 5-trimethoxybromobenzene 18

A mixture of 74g (0.32mol) of 4-bromo-2, 6-dimethoxy-phenol **17** and 32g (0.8mol) of NaOH in 850ml of H_2O was cooled to 10°C and 45ml (0.48mmol) of dimethyl sulfate was added. The mixture was refluxed for 3h and an equal amount of dimethyl sulfate (total 0.96mol) was then added. The mixture was refluxed for another 3h. Upon cooling overnight, the gray product solidified and was filtered off and dissolved in 1.2 l of ether. The ether solution was filtered to remove insoluble impurity and washed sequentially with 5% NaOH solution (200ml), water (2 X 200mL), and brine (200mL). The ether phase was dried over

Na_2SO_4 to give a off-white solid, which was recrystallized in hexane (300ml) to give 62.3g (79%) of **18**.

Synthesis of (3, 4, 5-trimethoxyphenyl)diphenylphosphine 19

To a solution of 3,4,5-trimethoxybromobenzene **18** (62.3g, 0.25mol) in dry THF (200ml) was added BuLi solution (169ml, 1.6M in hexane, 0.27mol) dropwise at –78°C within 45min. The resulting beige-colored suspension was stirred for an additional 1h at –78°C. Then PPh_2Cl (61g, 0.277mol, 49.7ml) was added dropwise. The addition was complete within 2h. The resulting yellow solution was allowed to warm to 0°C within 2h and quenched by addition of NH_4Cl solution (200ml). The organic layer was separated, washed with brine (250ml), dried (Na_2SO_4), filtered, and evaporated. The solid was recrystallized from methanol to give 69.5g(80%) of **19**.

Ref.: *Helvetica Chimica Acta* Vol. 74, **1991**, 370-389

Synthesis of 3, 4, 5-trimethoxyphenyl)diphenylphosphine oxide 20

To a suspension of **19** (69.5g, 0.2mmol) in MeOH (500 ml) was added dropwise 30% H_2O_2 (24.5g, 0.215mol) at 0°C. The resulting clear solution was stirred at ambient temperature for 1h. Then it was treated with sat. Na_2SO_3 solution (75 ml) and 1N HCl solution (50 ml). The mixture was concentrated under reduced pressure to remove the MeOH. The solid residue was dissolved in CH_2Cl_2 (300ml), washed with water (2x200 ml) and brine (200 ml), dried over Na_2SO_4, and evaporated. To the resulting white solid was added 300ml hexane and the resulting suspension was stirred vigorously at room temperature. Filtration of the white solid powder gave 67.2g (0.182mol, 91%) of pure **20**.

Ref: *Helvetica Chimica Acta* Vol. 74, **1991**, 370-389

Synthesis of (2-iodo-3,4,5-trimethoxyphenyl)diphenylphosphine oxide 21

To a solution of $(i\text{-}Pr)_2NH$ (31.88ml, 23.02g, 0.227mol) in dry THF (200ml)was added n-BuLi solution (125ml, 1.6M in hexane, 0.2mol) dropwise at –78°C. The addition was complete within 15min. After stirred at 0°C for 10min, the LDA solution was re-cooled to –78°C. It was then added via cannula to a flask containing a solution of **20** (67.2g, 0.182mol) in dry THF (200ml) over 20min. During the addition, the mixture was turned reddish-brown, and eventually a beige suspension was formed. After the reaction mixture was stirred for an additional 15min at –78°C, a solution of I_2 (50.6g, 0.2mol) in THF (200ml) was added dropwise. The addition was complete in 3h. A reddish-brown viscous paste was formed at the end of the addition. Then, the cooling bath was removed, and the mixture was allowed to warm to 0°C to form a clear red solution. The mixture was quenched by the addition of a $Na_2S_2O_3$ solution (12g in 100ml H_2O). The solution was concentrated to remove THF. The residue was dissolved in 300ml of CH_2Cl_2, washed with water (2 x 200 ml) and brine (200ml), dried over Na_2SO_4, and evaporated. The brown paste was recrystallized in EtOAc (100ml) to give 55g (62%) of **21**.

Ref: *Helvetica Chimica Acta* Vol. 74, **1991**, 370-389

Synthesis of (2-phenyl-3,4,5-trimethoxyphenyl)diphenylphosphine oxide 22

To a 2 liter Schlenk flask was added (2-iodo-3,4,5-trimethoxyphenyl) diphenylphosphine oxide **21** (30g, 61mmol), phenylboronic acid (11.1g, 91mmol), and degassed THF (800ml). A solution of degassed saturated K_2CO_3 (400ml) was added afterwards. The whole mixture was degassed with nitrogen for an additional 10min. Then, $Pd(PPh_3)_4$ (1.22mmol, 1.4g) was added in the solution through one portion. The mixture was stirred at reflux under nitrogen for 24hrs. In situ ^{31}PNMR showed that the reaction was complete. The reaction mixture was concentrated under reduced pressure to remove THF and 400ml of CH_2Cl_2 was

then added. The CH_2Cl_2 layer was washed with water (200ml) and brine (200ml), dried over Na_2SO_4, and evaporated. The solid residue was recrystallized from EtOAc (100ml) to give off-white product **22** (23g). The mother liquid was passed through a silica gel column to give another 4g of product **22**. The total yield was 98%.

Synthesis of (2-iodo-6-phenyl-3,4,5-trimethoxyphenyl)diphenylphosphine oxide 23

To a solution of (2-phenyl-3,4,5-trimethoxyphenyl)diphenylphosphine oxide **22** (26.5g, 59.7mmol) in dry THF (500ml) was added t-BuLi (47.7ml, 1.5M in pentane, 71.6mmol) dropwise at –90°C. The addition was complete within 2hrs. The solution was allowed to warm to –78°C and stirred for an additional 3h. Then a solution of I_2 in THF (100ml) was added dropwise at this temperature. The addition was complete in 2h. The resulting dark solution was allowed to warm to room temperature and stirred overnight. A solution of $Na_2S_2O_3$ (12g in 100ml H_2O) was added. The resulting yellow solution was concentrated under reduced pressure. To the residue was added 500ml of CH_2Cl_2. The CH_2Cl_2 layer was washed with water (100ml) and brine (100ml), dried over Na_2SO_4, and evaporated. The residue was recrystallized from EtOAc (100ml) to give a pure brown solid **23** (24g). The mother liquid was passed through a silica gel column to give another 5g of product. The total yield is 85%.

Synthesis of (RS)-(3,3'-diphenyl-4,4',5,5',6,6'-hexamethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide) 24

A mixture of (2-iodo-6-phenyl-3,4,5-trimethoxyphenyl)diphenylphosphine oxide **23** (7.4g, 12.6mmol), Cu powder (252mmol, 16g, activated by I_2 treatment), and DMF (200ml) was stirred at 155°C for 1hr. The cold mixture was evaporated to dryness at the rotor evaporator at 70°C. The residue was treated for a few min with CH_2Cl_2 (200ml). The solid was removed by filtration and washed with

CH_2Cl_2 (200ml). The combined filtrate was washed with sat. NH_4Cl solution (2 X 100mL), dried over Na_2SO_4, and evaporated. The residue was crystallized from EtOAc (100ml) to give 5g (90%) of white product **24.**

Resolution of (3,3'-diphenyl-4,4',5,5',6,6'-hexamethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide) 25

To a mixture of (RS)-(3,3'-diphenyl-4,4',5,5',6,6'-hexamethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide) **24** (2.3g, 2.5mmol) and (-)-DTTA (-0.966g, 2.5mmol) was added 40ml of i-PrOH. The resulting slurry was heated to reflux to get a clear solution. Then it was cooled slowly to room temperature and stirred overnight. The salt of (-)-**25** and (-)-DTTA was obtained as white powder through filtration(ee: 95%). The salt was recrystallized one more time from 25ml i-PrOH and 1.1g of solid was obtained. The solid was dissolved in 50ml of CH_2Cl_2, washed with 3N NaOH (2x 50ml) and water (3x 50mL), dried over Na_2SO_4, and evaporated. The solid (97.7%, 0.86g) was recrystallized from acetone to give enantiomerically pure product **25** (0.69g, 60%, ee>99.5%).

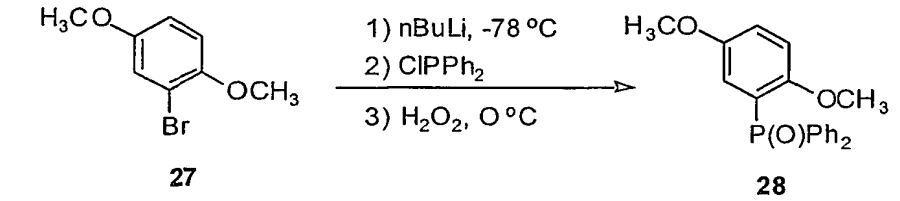
Synthesis of (-)-(3,3'-diphenyl-4,4',5,5',6,6'-hexamethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine) 26.

To a solution of (-)-(3,3'-diphenyl-4,4',5,5',6,6'-hexamethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide) **25** (700mg, 0.79mmol, resolved from (-)-DTTA), tributylamine (6.5ml, 27.3mmol), and xylene (100 ml) was added $HSiCl_3$ (1.72 ml, 17mmol) dropwise at 0°C. The reaction was stirred at reflux for 2days. Some precipitates came out during the course. After cooled down, the reaction mixture was quenched with 30% degassed NaOH solution (20ml) in an ice-water bath. The resulting solution was kept at 60°C for 1h. The organic phase was transferred into another Schlenk flask through cannula. The water phase was re-washed with CH_2Cl_2 (30ml*2). The combined organic phase was washed with water (50 ml), dried over Na_2SO_4, and evaporated under reduced pressure. The

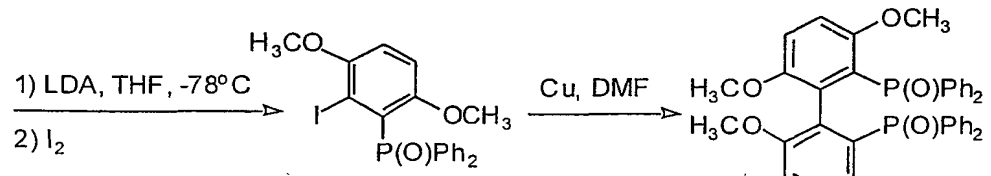
resulting yellow residue was dissolved in CH_2Cl_2 (10 ml) and passed through a basic Al_2O_3 column to give a pure white solid **26** (400 mg, 59%).

EXAMPLE 11

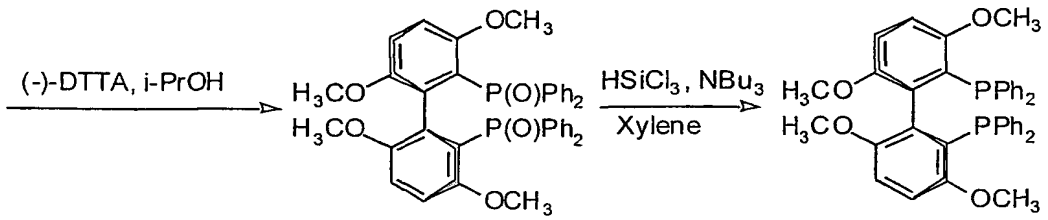
Synthesis of 2,2'-(diphenylphosphanyl)-3, 6, 3',6'-tetramethoxybiphenyl



27 **28**



29 **30**



31 **32**

(2,5-Dimethoxyphenyl)diphenylphosphine oxide

At –78°C, 2.5M n-BuLi in hexane (48mL, 0.12mol) was slowly added to a solution of 1-Bromo-2,5-dimethoxybenzene (**27**, 25g, 0.115mol) in THF (250mL) causing the solution to become dark yellow (solid suspension). The reaction mixture was stir at this temp for about 30 minutes, following by addition of

diphenylchlorophosphine (21.5 ml, 0.12 mol). During the addition, control the temp below –50°C (add slowly). The resulting yellow solution was allowed to warm up to room temp (take about two hours). The saturated NH_4Cl solution (200 ml) was added and reaction mixture form two layers. The organic layer was washed with brine (2×100mL) and dried (Na_2SO_4). The solvent was removed under vacuum to give a white solid.

Add MeOH (200mL) to the resulting white solid to form suspension. At 0°C, 33% H_2O_2 (14ml, 0.13mol) was slowly added to above MeOH suspension. The addition process takes about 20 minutes and the solid vanished promptly after all H_2O_2 was added. The mixture was allowed to stir for one hour at 0°C, follow by adding saturated $NaHSO_3$ solution (15ml) and stir for 30 minutes (the KI-Starch paper was applied here to make sure all peroxide was reduced). The solvent was removed under vacuum to give a white solid. The resulting solid was dissolved in CH_2Cl_2 (200mL) and was washed with water (150mL) and brine (150mL), dried (Na_2SO_4). The solvent was also removed under vacuum to give a white solid. The crude product was treated with hot hexane (2×100mL) (to remove trace amount of impurity) to give pure product (**28**, 37.3g, 95.8%).

(3,6-Dimethoxy-2-iodophenyl)diphenylphosphine oxide

A solution of LDA (6mmol) 1.5M in pentane was slowly added to the phosphine oxide (**28**, 1.69g, 5mmol) in THF (60mL) at 100°C. The resulting dark yellow solution (solid suspension) was allowed to warm up to –78°C (take 30 minutes) and then stirred 3.5 hours at this temp. during which time the white solid precipitated. Solid I_2 (1.78g, 7mmol) was added against a counter flow of N_2 to the anion in THF at –78°C. The reaction was allowed to come to 0°C and quenched with $Na_2S_2O_3$ aq. solution (10mL). The solvent was removed under vacuum and the residue was extracted with CH_2Cl_2 (50mL), washed with water (50mL), brine (50ml) and dried (Na_2SO_4). The solvent was removed and the brown oil residue was treated with EtOAc (10mL) (to wash out most of the color

impurities, the product form white solid in EtOAc). Then the vacuum filtration gives the white solid (**29**, 1.0g, 43%)

2,2'-(Diphenylphosphinoyl)3,3',6,6'-tetramethoxybiphenyl

Copper powder (320mg, 5mmol) was added to a solution of the iodide (**29**, 116mg, 0.25mmol) in DMF (10mL) and the reaction mixture heated to reflux for 8 hours. During the reflux, white solid formed along the wall of flask. The mixture was treated under vacuum to remove most of the solvent (before it cooled). The residue was extracted with CH_2Cl_2 (20mL) and washed with water (2×10mL), brine (10mL) and dried (Na_2SO_4). The solvent was removed under vacuum and the resulting solid was washed with EtOAc (2mL) to give a white solid (**30**, 70mg, 83%).

Resolution of 2,2'-(diphenylphosphinoyl)3,3',6,6'-tetramethoxybiphenyl

(-) DTTA (0.579g, 1.5mmol) was added to diphosphine oxide (**30**, 0.674g, 1mmol) in EtOH (29mL) solution(at this time, DTTA can not dissolve in EtOH solution). The reaction mixture was heated up to reflux until all solid suspension was completely dissolved (take about 20 minutes). The resulting solution was allowed to stir overnight until crystal formed. The mixture was filtrated under vacuum and washed with cold EtOH (5mL). The resulting solid (0.405g, 75.1%) was added to CH_2Cl_2 (20mL) and NaOH (20mL, 10% aq.) solution for about 5 minutes, and the entire insoluble solid disappeared. The organic layer was washed with water (2×10mL), brine (10mL) and dried (Na_2SO_4). The solvent was removed under vacuum to give a white solid (**31**, 99.3% ee).

2,2'-Diphenylphosphanyl-3,6,3',6'-tetramethoxybiphenyl

$HSiCl_3$ (542mg, 0.4mL) and NBu_3 (1.48g, 1.9mL) were added to diphosphine oxide (**31**, 70mg, 0.1mmol) in xylene (5mL) solution under N_2

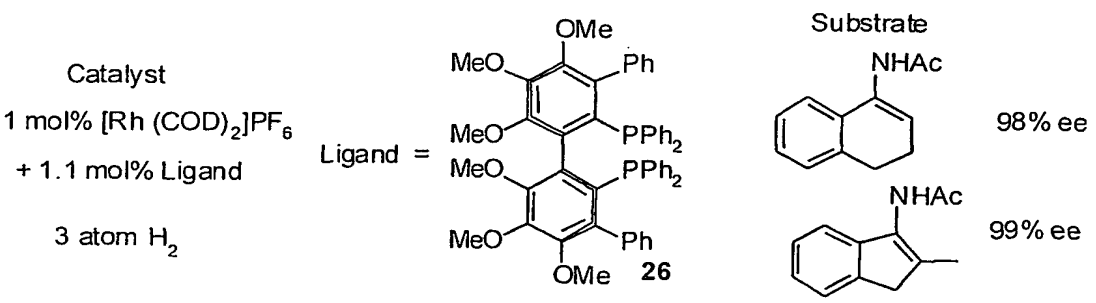
atmosphere. The reaction mixture was heated to reflux for 3 hours. The mixture was allowed to cool down to room temp. Then the degassed NaOH aq. solution (10%, 5mL) was added to reaction mixture at 0°C and stir for one hour. The organic layer was washed with degassed water (2×10mL), NH_4Cl aq. solution (10mL), brine (10mL) and dried (Na_2SO_4). The solvent was removed under vacuum to give a pale yellow solid. After a short plug (silica gel, elute with CH_2Cl_2:Hexane=1:1), the solvent was evaporated under vacuum to give a white solid (still not pure white, a little bit pale yellow color) (**32**, 50mg, 75%).

EXAMPLE 12

Asymmetric Hydrogenation of Enamides Facilitated by Rh-Complexes with (-) (3, 3'-diphenyl-4,4',5,5', 6, 6'-hexamethoxybiphenyl-2,2'-diyl)bis-(diphenylphosphine) (26)

Rh-complexes with (-) (3, 3'-diphenyl-4,4',5,5', 6, 6'-hexamethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine) (**26**) are good catalysts for hydrogenation of enamides. Introduction of 3, 3' substituted groups have some effects on enantioselectivity of asymmetric hydrogenation of enamides. Cyclic enamides can be hydrogenated with good enantioselectivity.

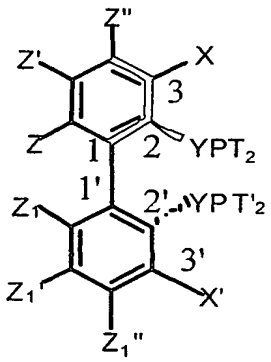
Rh-Catalyzed Asymmetric Hydrogenation



The present invention has been described with particular reference to the preferred embodiments. It should be understood that the foregoing descriptions and examples are only illustrative of the invention. Various alternatives and modifications thereof can be devised by those skilled in the art without departing from the spirit and scope of the present invention. Accordingly, the present invention is intended to embrace all such alternatives, modifications, and variations that fall within the scope of the appended claims.

WHAT IS CLAIMED IS:

1. A ligand represented by the formula or its enantiomer:



wherein each X and X' is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

wherein each Z and Z_1 is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$; or wherein Z and Z_1 together form the bridging group A-B-A_1;

wherein each Z', Z", Z_1' and Z_1" is independently selected from the group consisting of: H, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$; or wherein Z' and Z together form the bridging group A'-B-A; Z' and Z together form a fused cycloaliphatic or aromatic group; Z_1 and Z_1' together form the bridging group A_1-B_1-A_1'; and/or Z_1 and Z_1' together form a fused cycloaliphatic or aromatic group;

wherein each A, A', A_1 and A_1' is independently selected from the group consisting of: O, CH_2, NH, NR, S, CO and a bond;

wherein each B and B_1 is independently selected from the group consisting of: linear, branched or cyclic alkylene of 1 to 6 carbon atoms, arylene of 6 to 12

carbon atoms, O, CH_2, NH, NR, S, CO, SO_2, P(O)R, P(O)OR, POR, SiR_2 and a bond;

wherein each T is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R", YR', YR", Y'R' and Y"R"; or wherein two T groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

wherein each T' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R", YR', YR", Y'R' and Y"R"; or wherein two T' groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

wherein each R, R' and R" is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, aralkyl and alkaryl of 1 to 22 carbon atoms; or wherein two R groups, two R' groups or two R" group together form an alkylene, arelene or substituted arylene group; and

wherein each Y, Y' and Y" is independently selected from the group consisting of: O, CH_2, NH, S and a bond between carbon and phosphorus; with the proviso that when the Y group at the 2' position is a bond between carbon and phosphorus, X' is hydrogen.

2. The ligand of claim 1, wherein said substituted alkyl has one or more substituents, each independently selected from the group consisting of: halogen, ester, ketone, carboxylic acid, hydroxy, alkoxy, aryloxy, thiol, alkylthio and dialkylamino.

3. The ligand of claim 1, wherein said alkylene is selected from the group consisting of compounds represented by the formula: $-(CH_2)_n-$, wherein n is an integer in the range of from 1 to 8.

4. The ligand of claim 1, wherein each of said aryl groups optionally has one or more substituents, each independently selected from the group consisting of: halogen, ester, ketone, sulfonate, phosphonate, hydroxy, alkoxy,

aryloxy, thiol, alkylthiol, nitro, amino, vinyl, substituted vinyl, carboxylic acid, sulfonic acid and phosphine.

5. The ligand of claim 1, wherein each of said arylene groups optionally has one or more substituents, each independently selected from the group consisting of: halogen, ester, ketone, sulfonate, phosphonate, hydroxy, alkoxy, aryloxy, thiol, alkylthiol, nitro, amino, vinyl, substituted vinyl, carboxylic acid, sulfonic acid and phosphine.

6. The ligand of claim 1, wherein each of said arylene groups is independently selected from the group consisting of: 1,2-divalent phenyl, 2,2'-divalent-1,1'-biphenyl, 2,2'-divalent-1,1'-binaphthyl and ferrocene.

7. The ligand of claim 1, wherein said ligand is a racemic mixture of enantiomers.

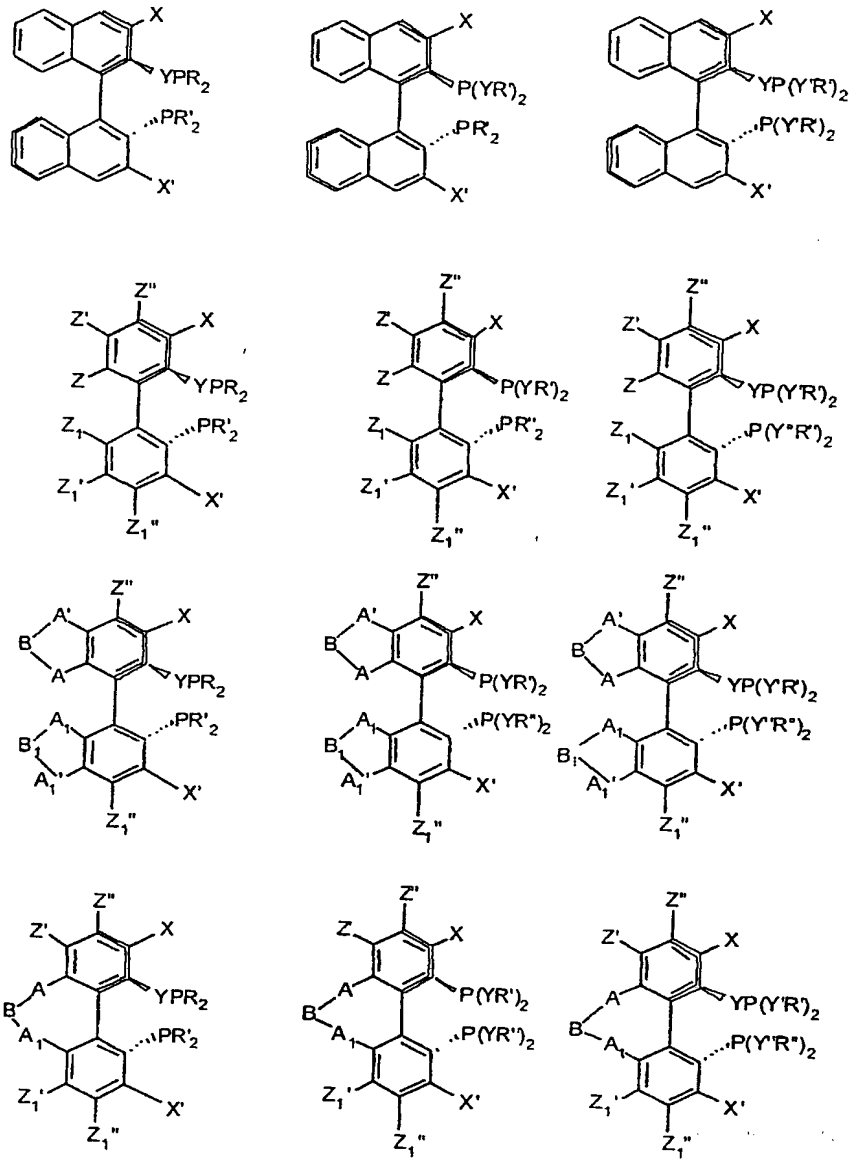
8. The ligand of claim 1, wherein said ligand is a non-racemic mixture of enantiomers.

9. The ligand of claim 1, wherein said ligand is one of the enantiomers.

10. The ligand of claim 1, having an optical purity of at least 85% ee.

11. The ligand of claim 1, having an optical purity of at least 95% ee.

12. The ligand of claim 1, wherein said ligand is selected from the group consisting of compounds represented by the following formulas:



wherein each X and X' is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

wherein each Z and Z_1 is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide,

SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$; or wherein Z and Z_1 together form the bridging group A-B-A_1;

wherein each Z', Z", Z_1' and Z_1" is independently selected from the group consisting of: H, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$; or wherein Z' and Z together form the bridging group A'-B-A; Z' and Z together form a fused cycloaliphatic or aromatic group; Z_1 and Z_1' together form the bridging group A_1-B_1-A_1'; and/or Z_1 and Z_1' together form a fused cycloaliphatic or aromatic group;

wherein each A, A', A_1 and A_1' is independently selected from the group consisting of: O, CH_2, NH, NR, S, CO and a bond;

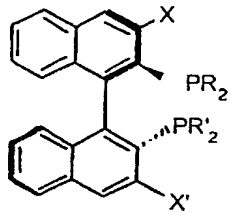
wherein each B and B_1 is independently selected from the group consisting of: linear, branched or cyclic alkylene of 1 to 6 carbon atoms, arylene of 6 to 12 carbon atoms, O, CH_2, NH, NR, S, CO, SO_2, P(O)R, P(O)OR, POR, SiR_2 and a bond;

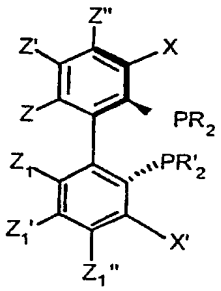
wherein each YR', YR", Y'R' and Y"R" is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide and aryloxide; or wherein two YR', YR", Y'R' or Y"R" groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

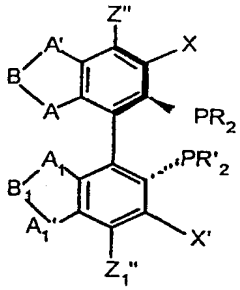
wherein each R, R' and R" is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, aralkyl and alkaryl of 1 to 22 carbon atoms; or wherein two R groups, two R' groups or two R" group together form an alkylene or arelene group; and

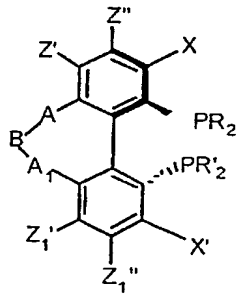
wherein each Y, Y' and Y" is independently selected from the group consisting of: O, CH_2, NH, S and a bond between carbon and phosphorus; with the proviso that when the Y group at the 2' position is a bond between carbon and phosphorus, X' is hydrogen.

13. The ligand of claim 1, wherein said ligand is selected from the group consisting of compounds represented by the following formulas:









5

wherein each X is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

wherein each X' is independently selected from the group consisting of: hydrogen, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

wherein each Z and Z_1 is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

wherein each Z', Z", Z_1' and Z_1" is independently selected from the group consisting of: H, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

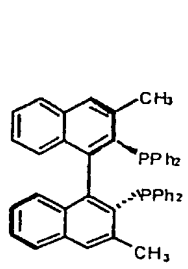
wherein each A, A', A_1 and A_1' is independently selected from the group consisting of: O, CH_2, NH, NR, S, CO and a bond;

wherein each B and B_1 is independently selected from the group consisting of: linear, branched or cyclic alkylene of 1 to 6 carbon atoms, arylene of 6 to 12 carbon atoms, O, CH_2, NH, NR, S, CO, SO_2, P(O)R, P(O)OR, POR, SiR_2 and a bond;

wherein each R and R' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, aralkyl and alkaryl of 1 to 22 carbon atoms, alkoxide and aryloxide; or

wherein two R groups or two R' groups together form an alkylene, arelene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl groups.

14. The ligand of claim 1, wherein said ligand is selected from the group consisting of compounds represented by the formulas:



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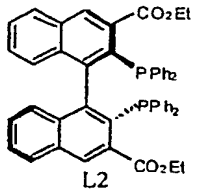

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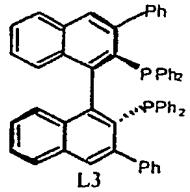

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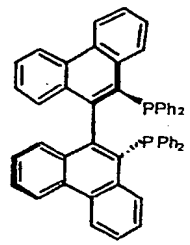

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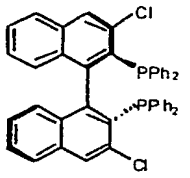

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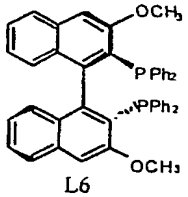

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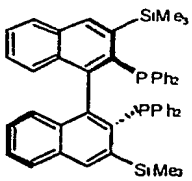

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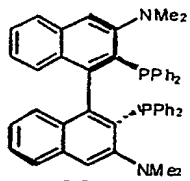

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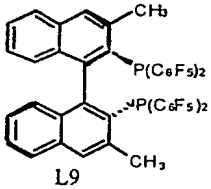

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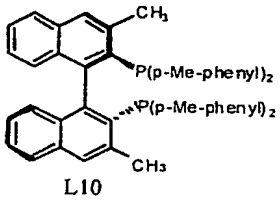

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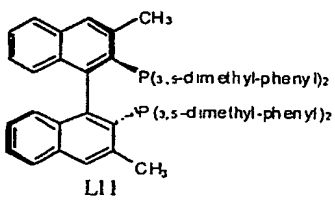

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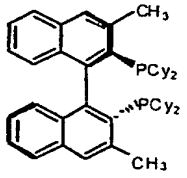

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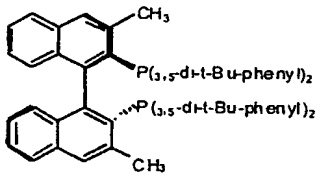

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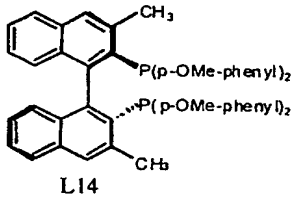

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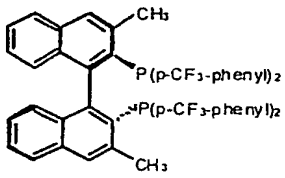

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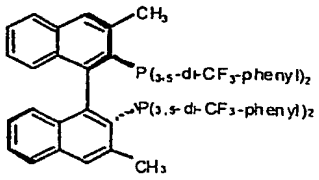

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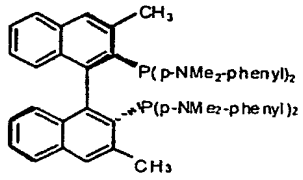

L17

5

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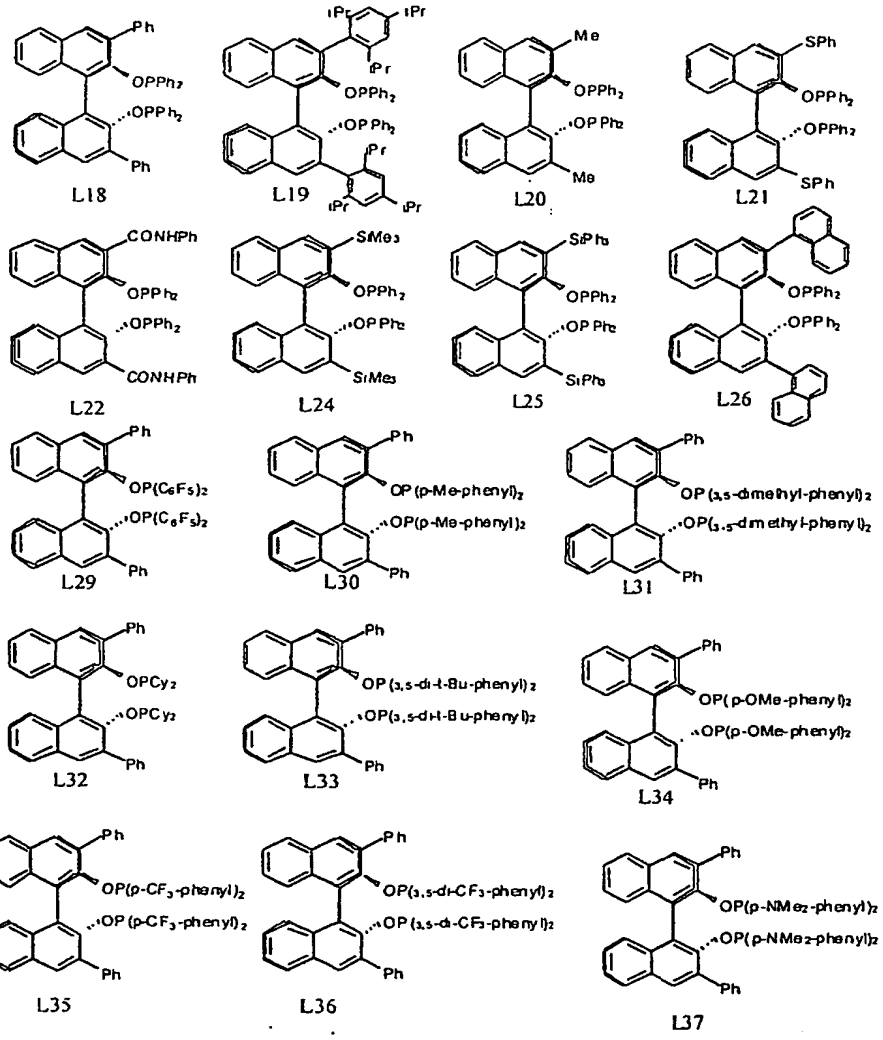

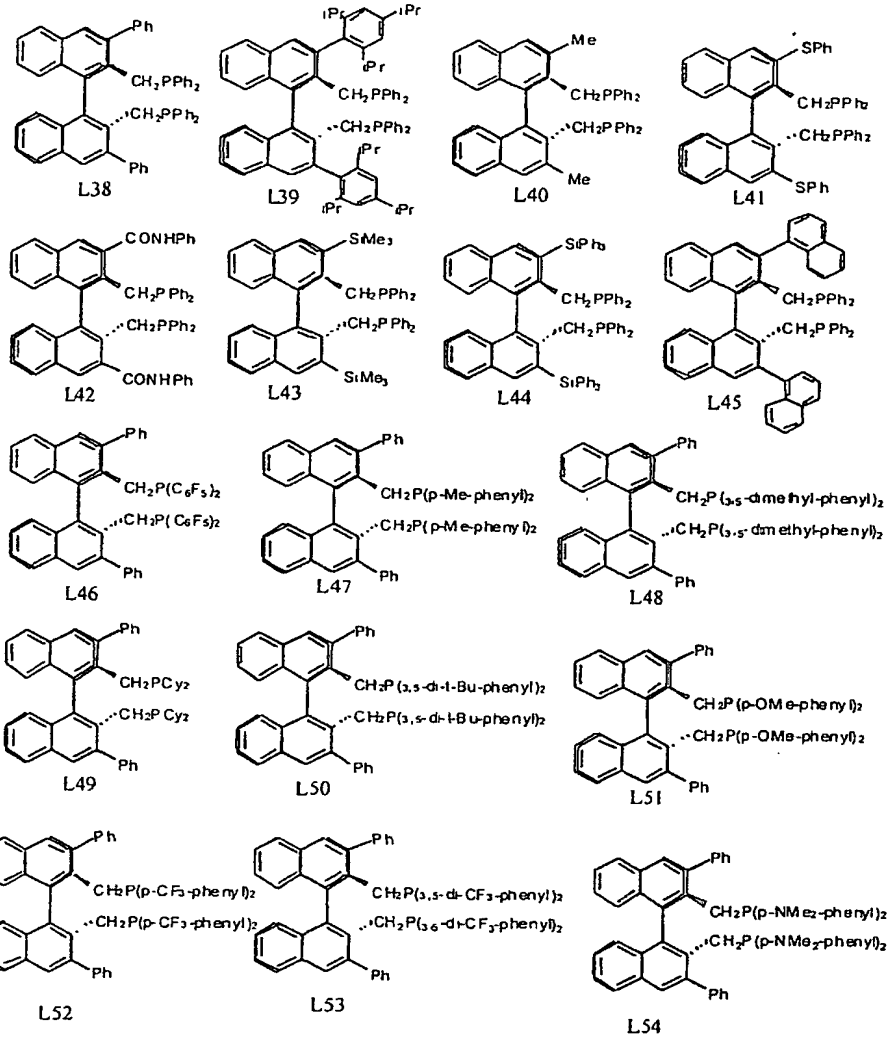

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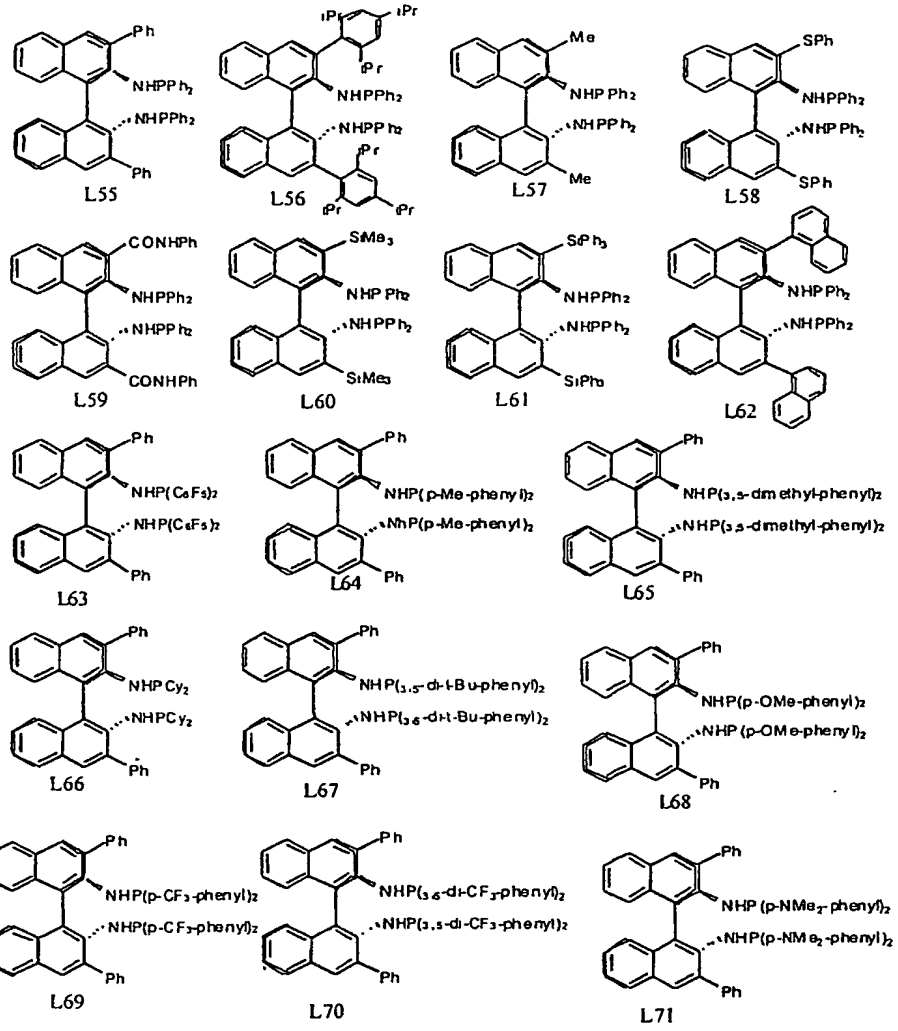

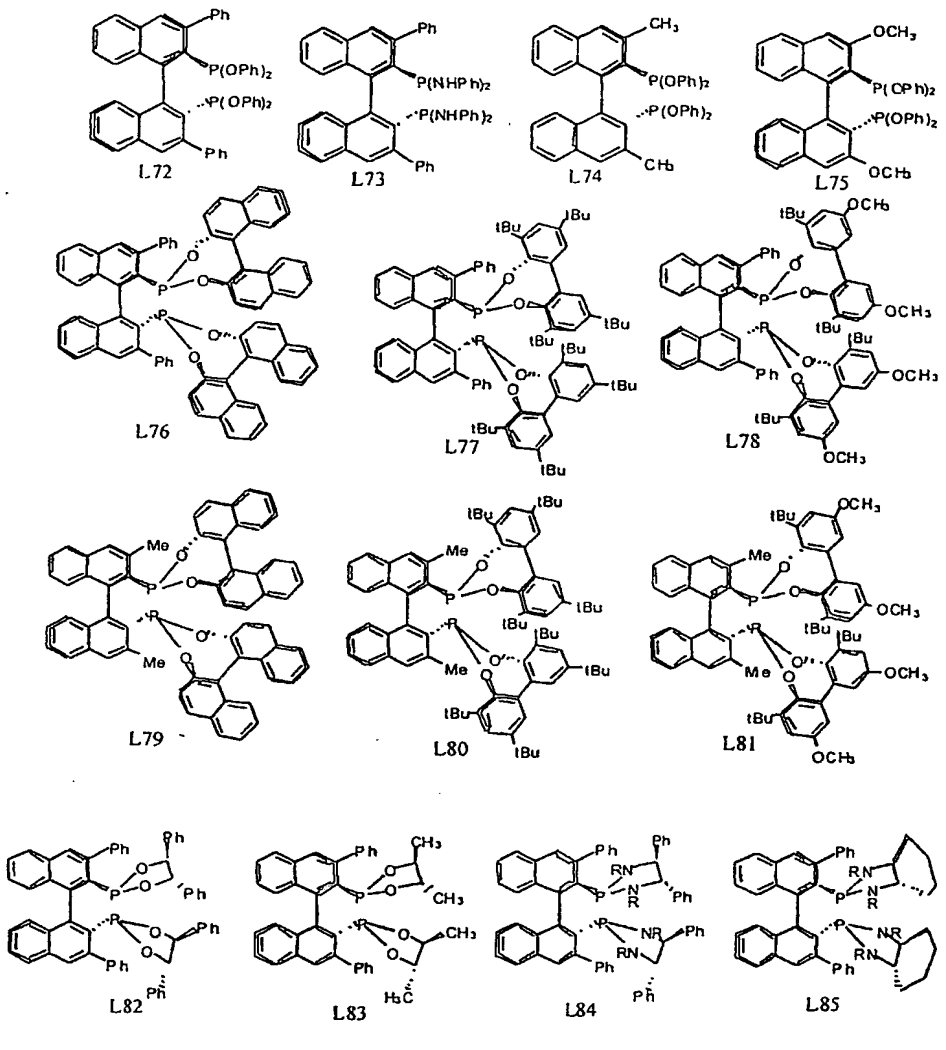

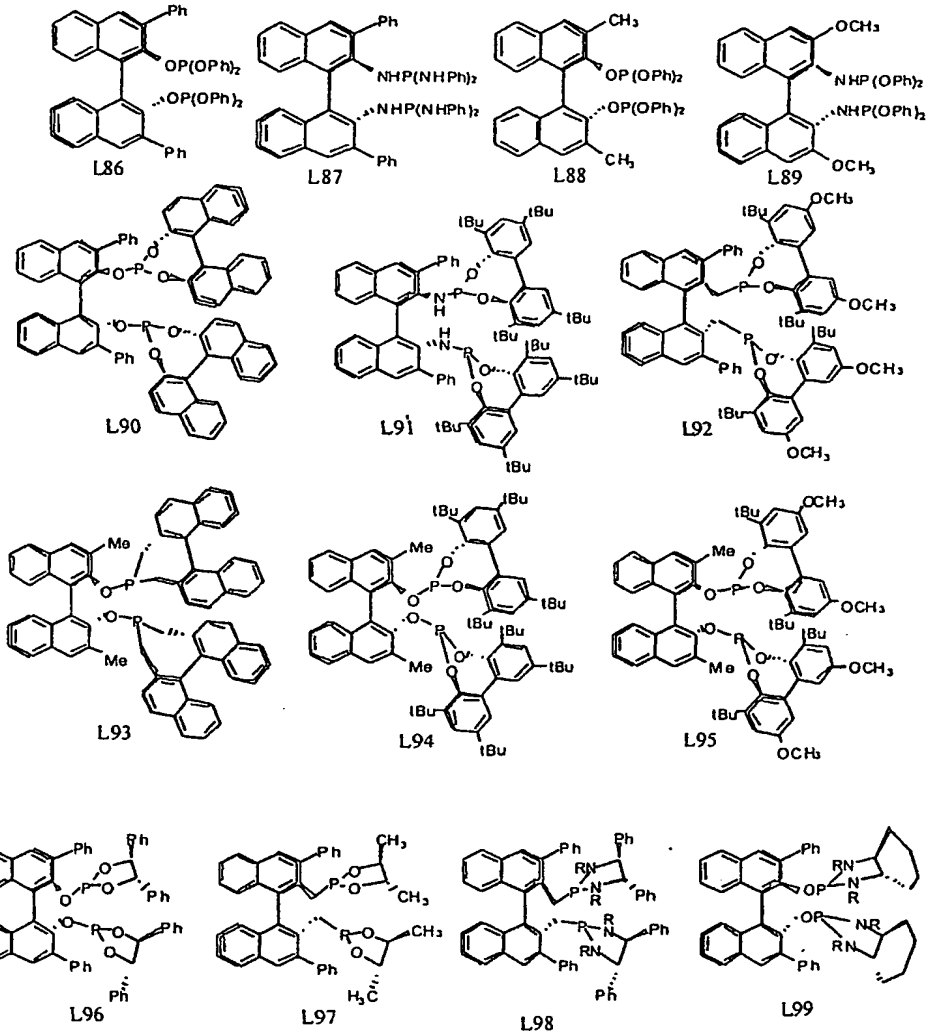

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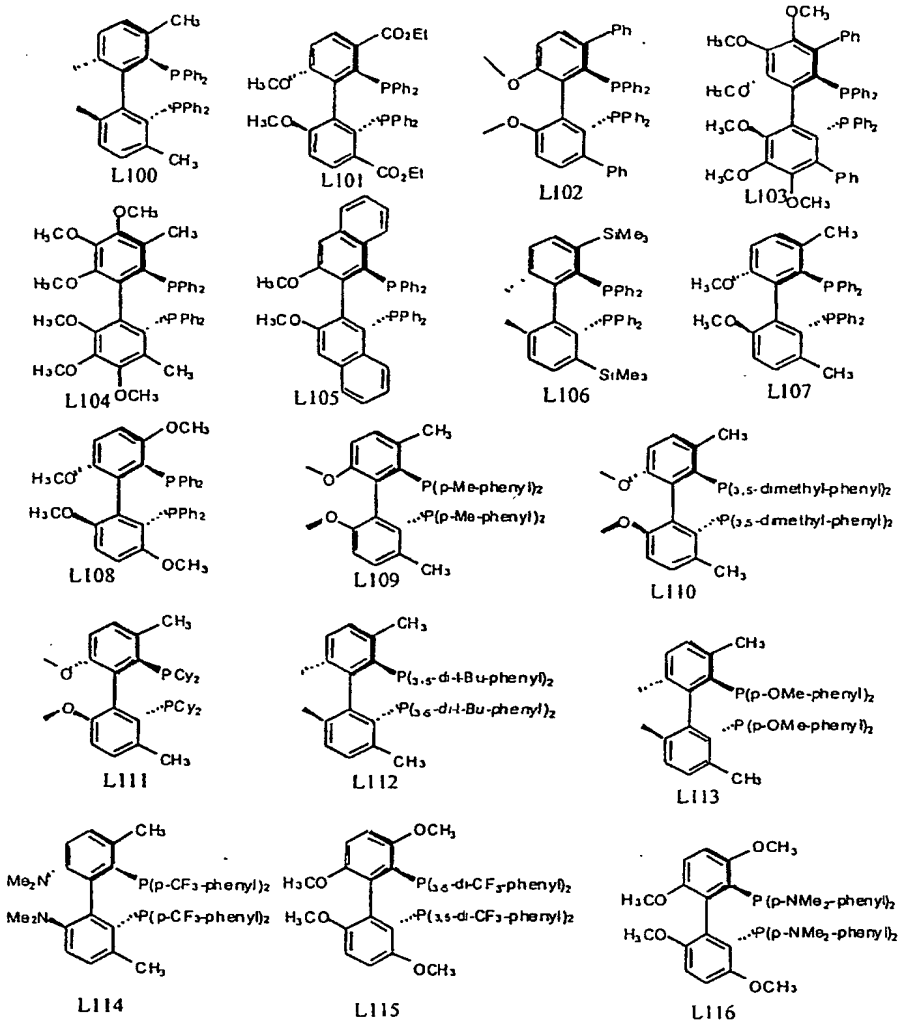

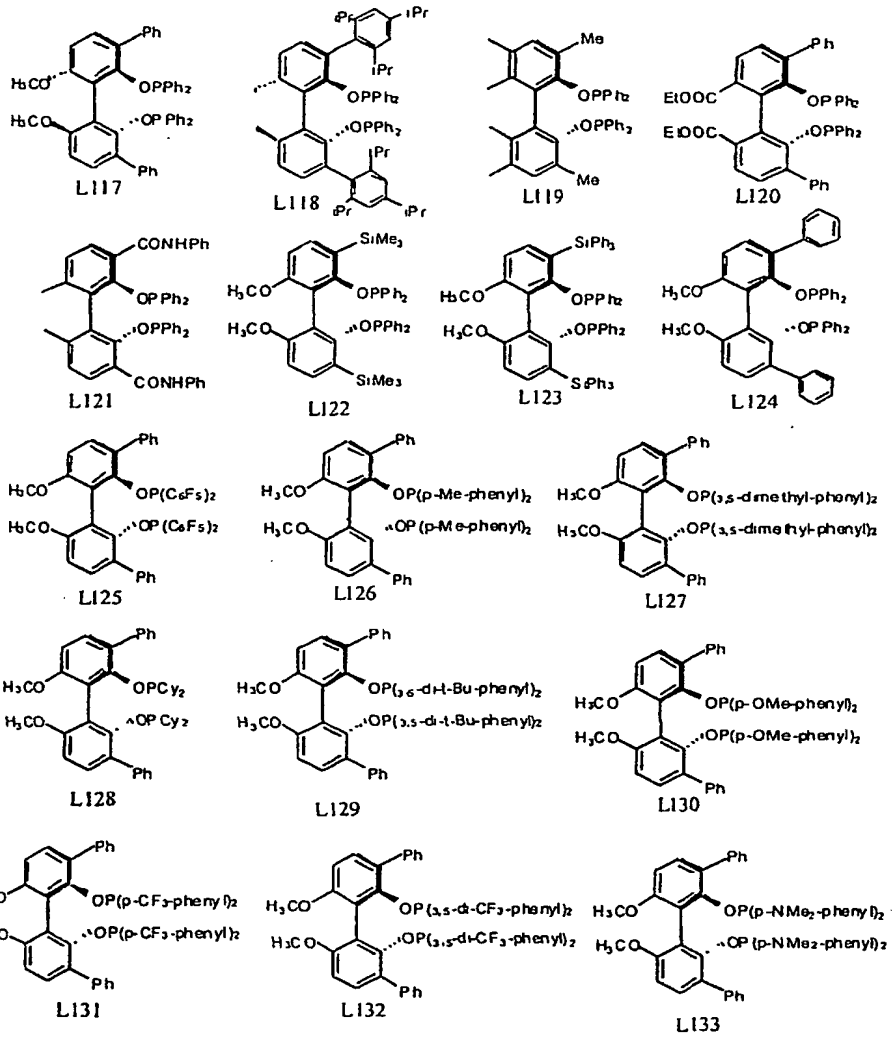

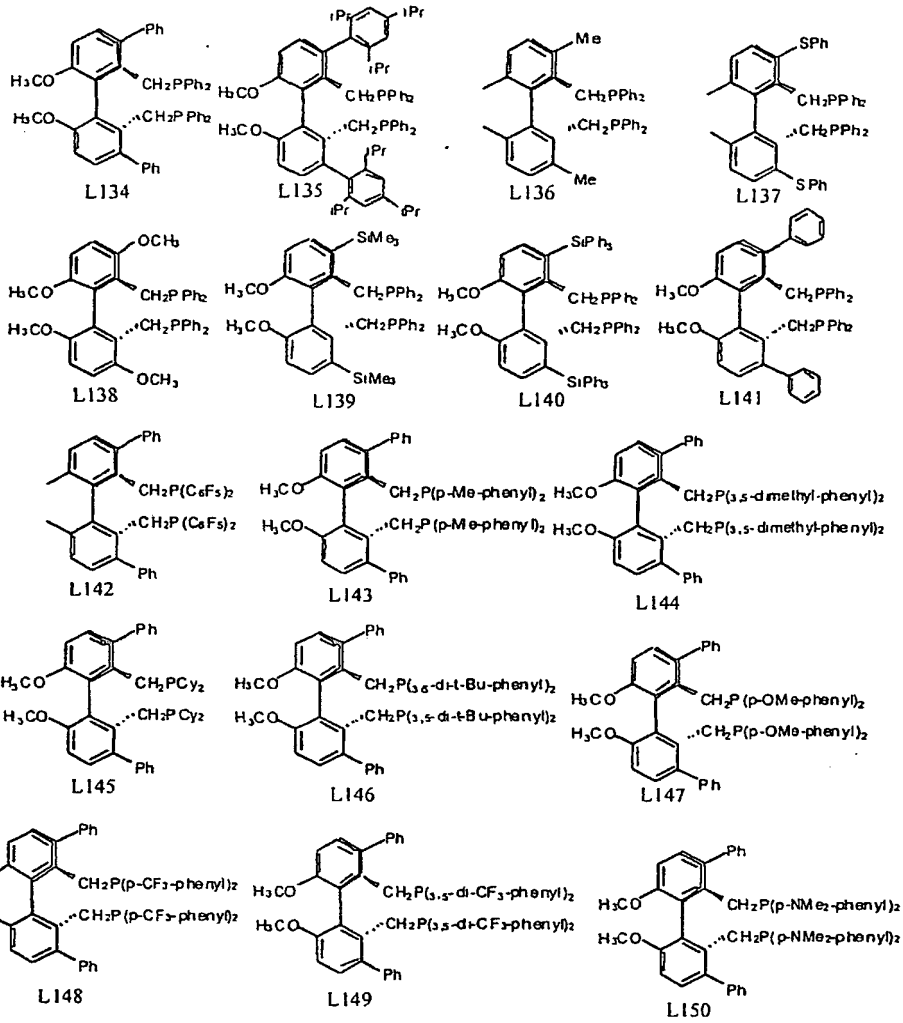

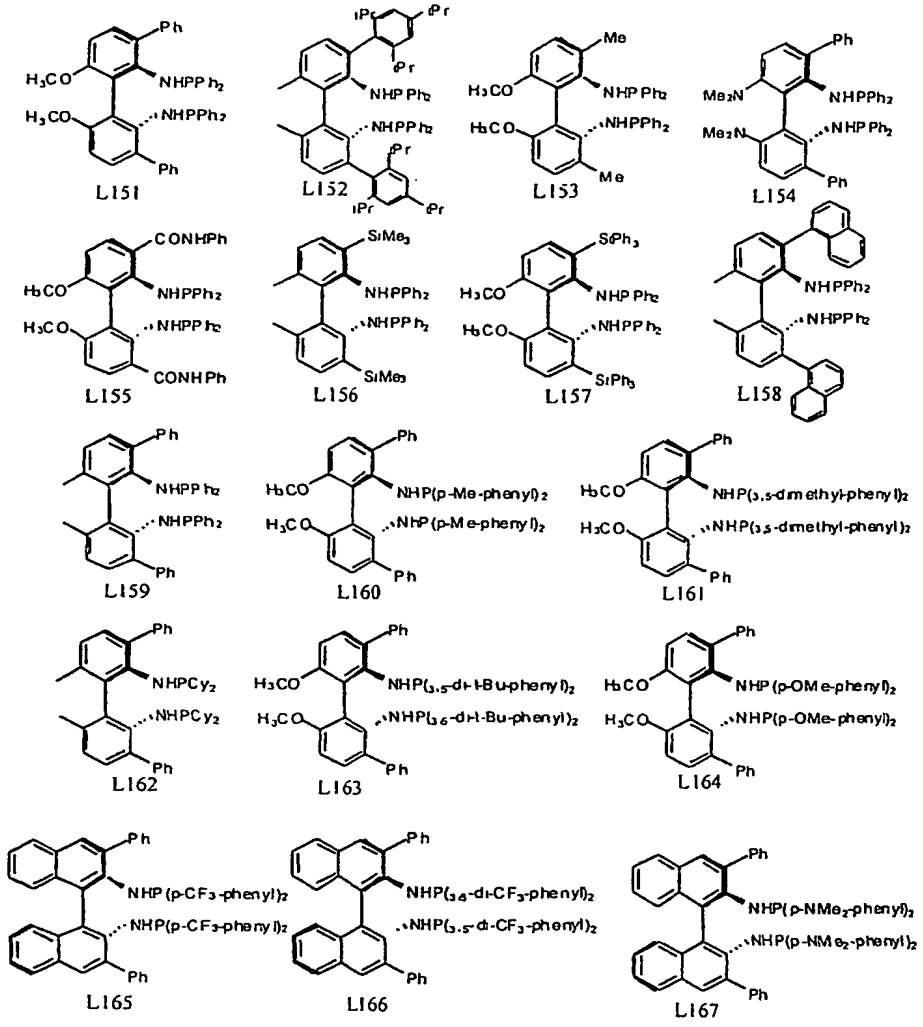

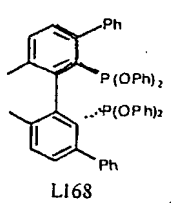
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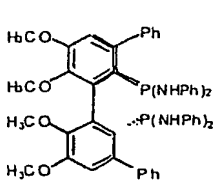
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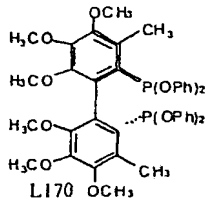
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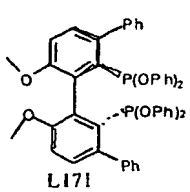
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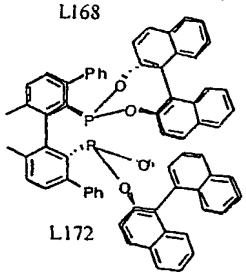
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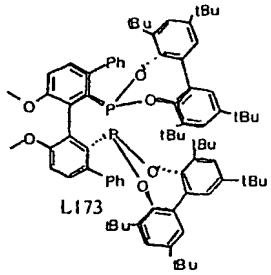
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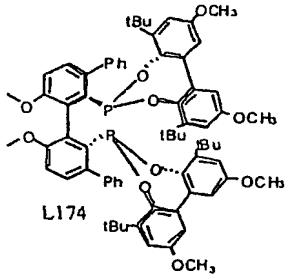
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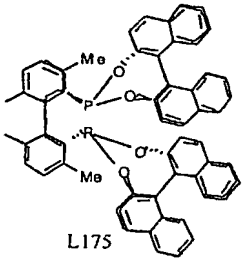
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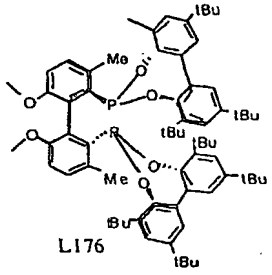
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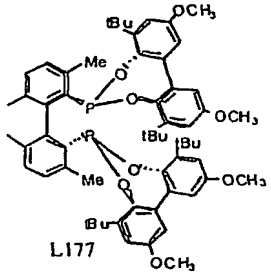
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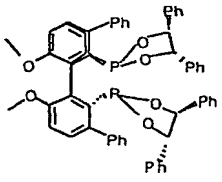
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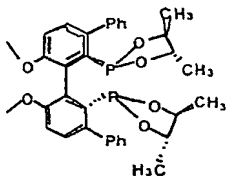
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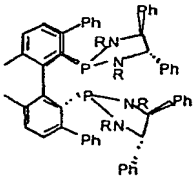
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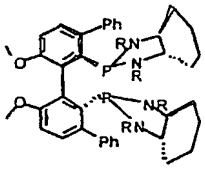
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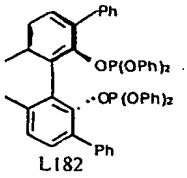
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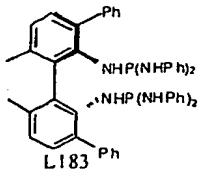
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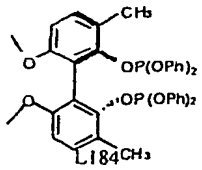
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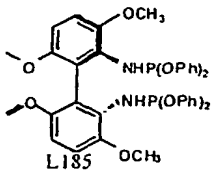
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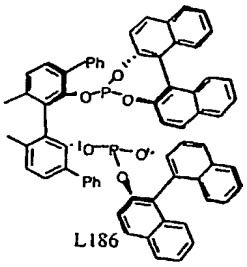
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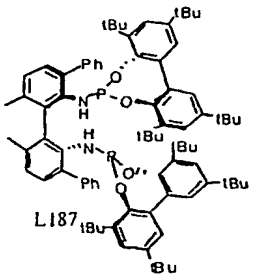
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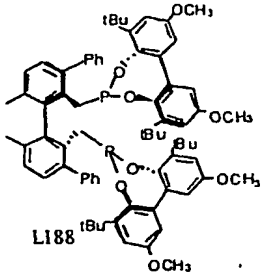
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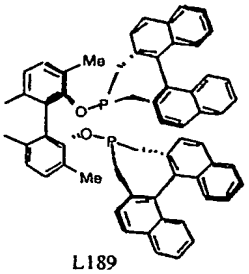
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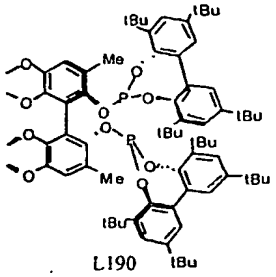
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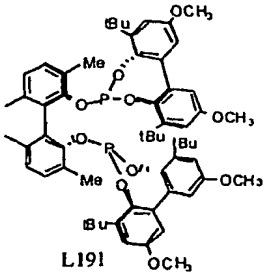
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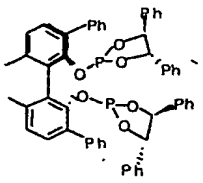
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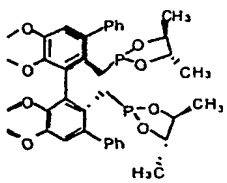
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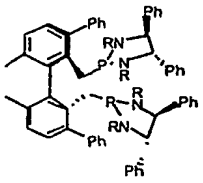
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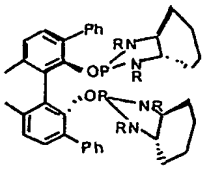
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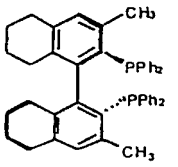

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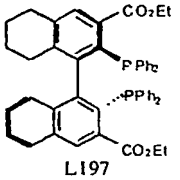

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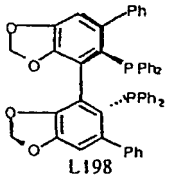

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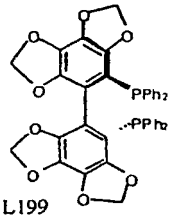

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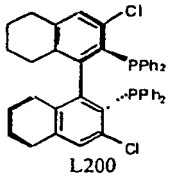

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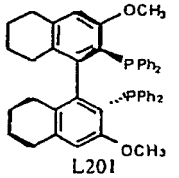

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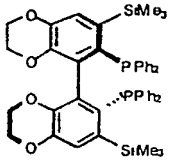

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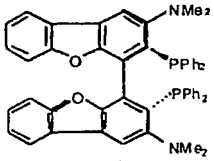

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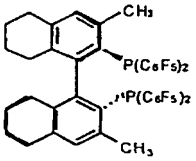

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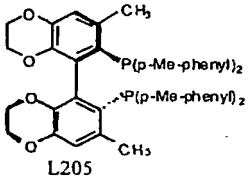

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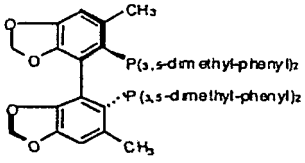

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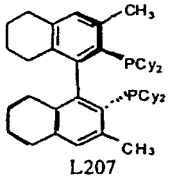

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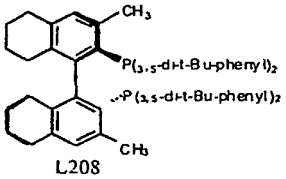

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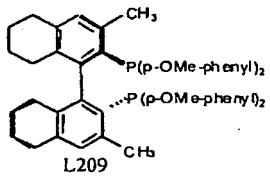

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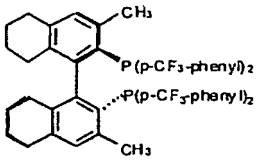

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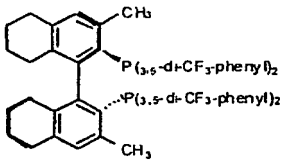

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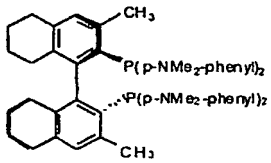

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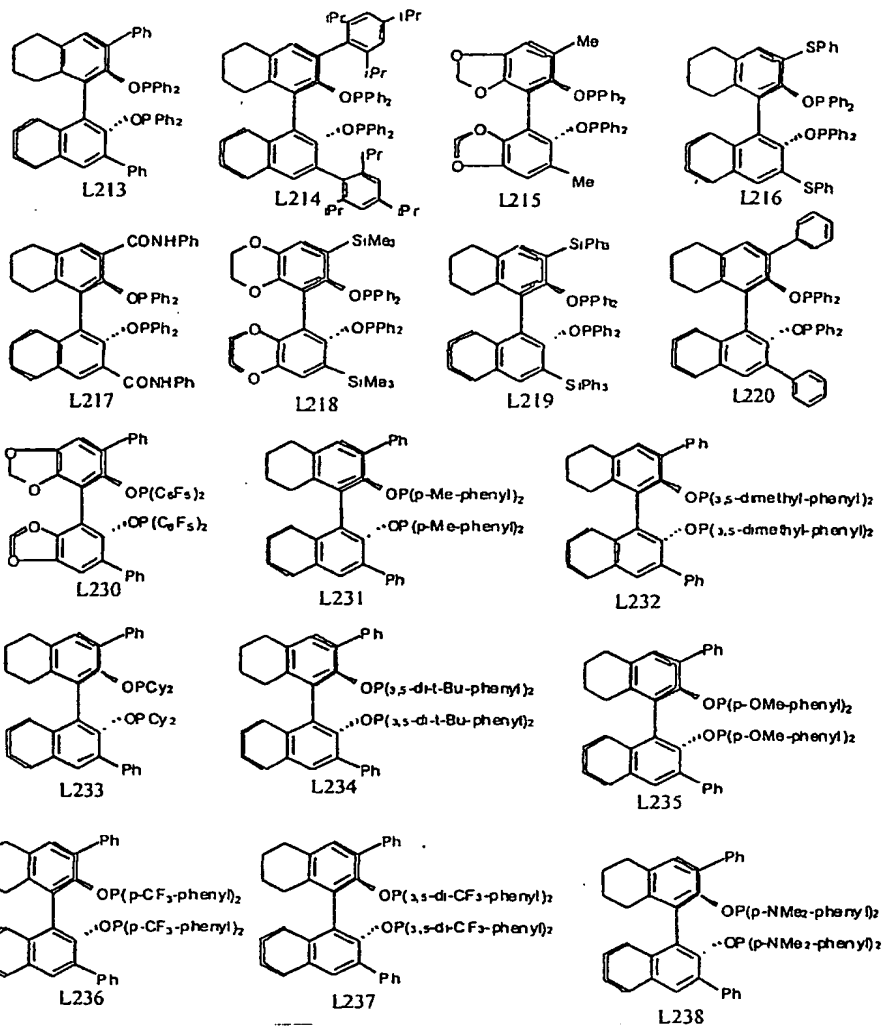

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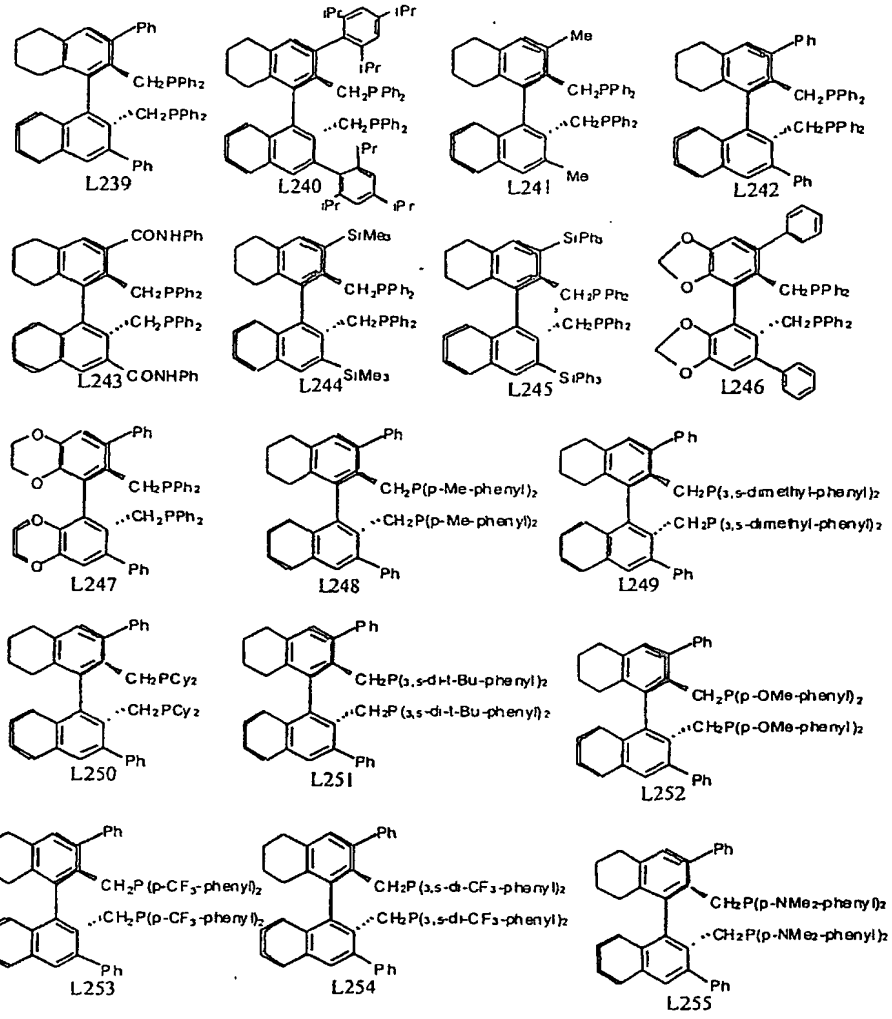

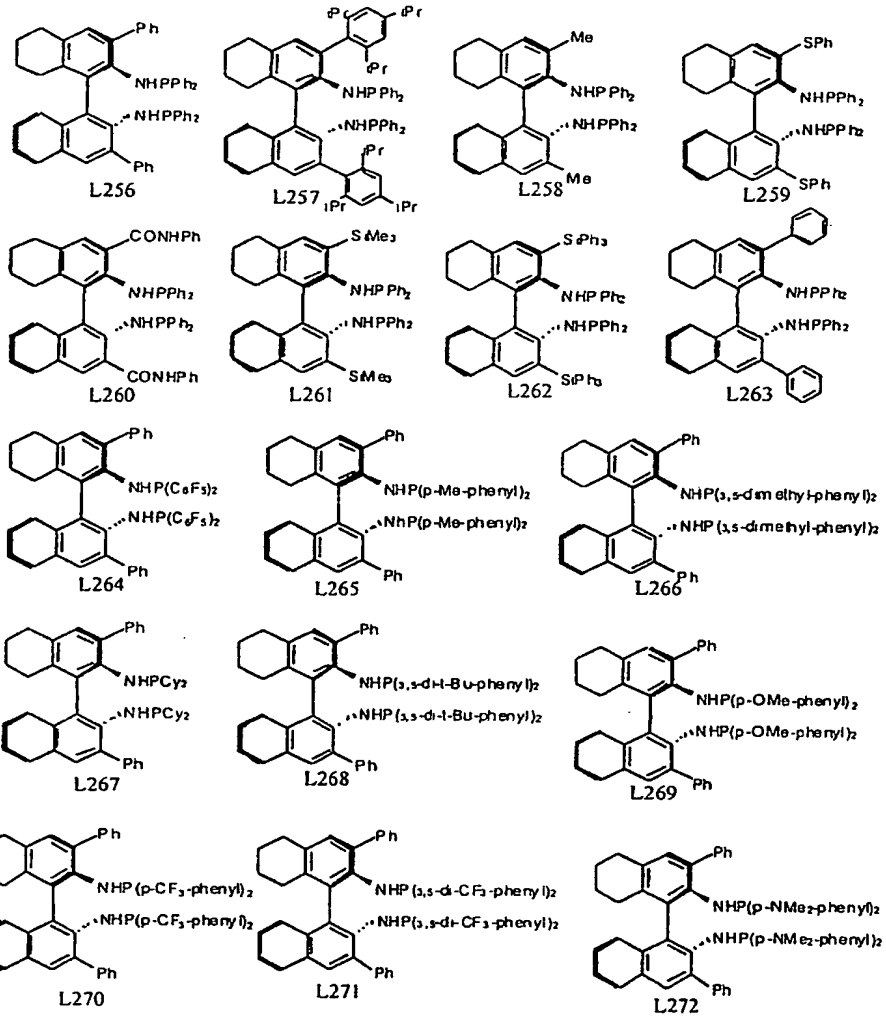

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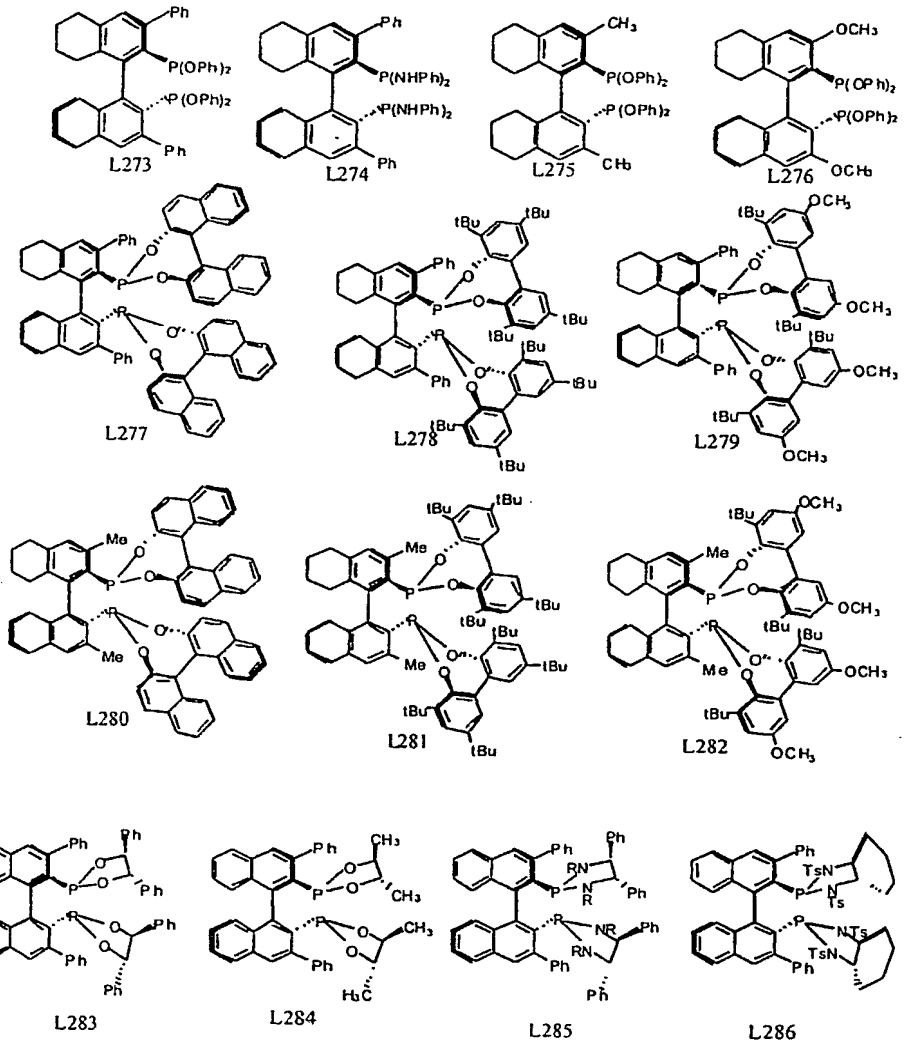

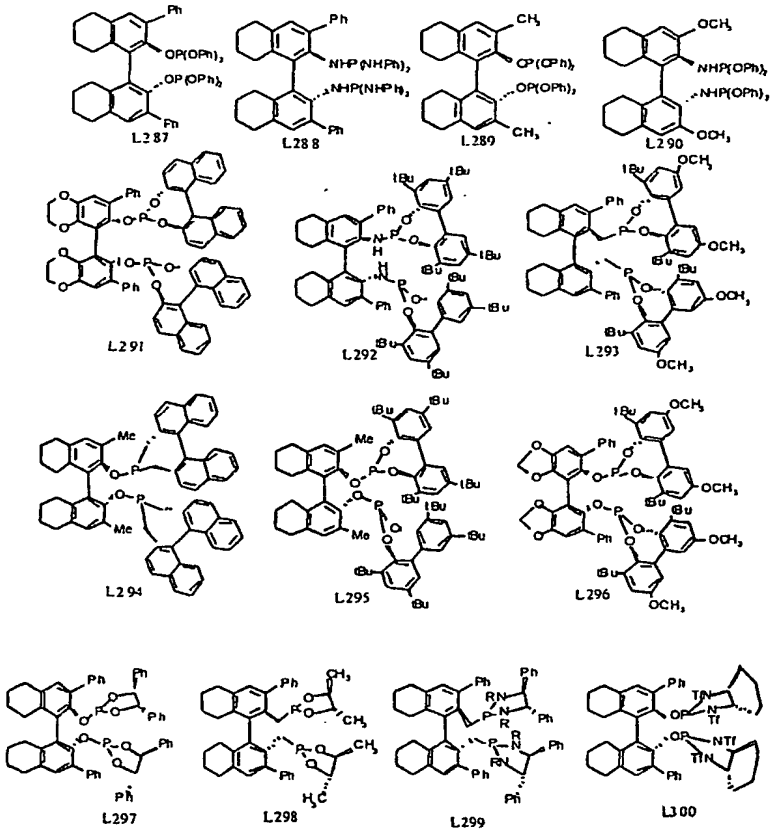

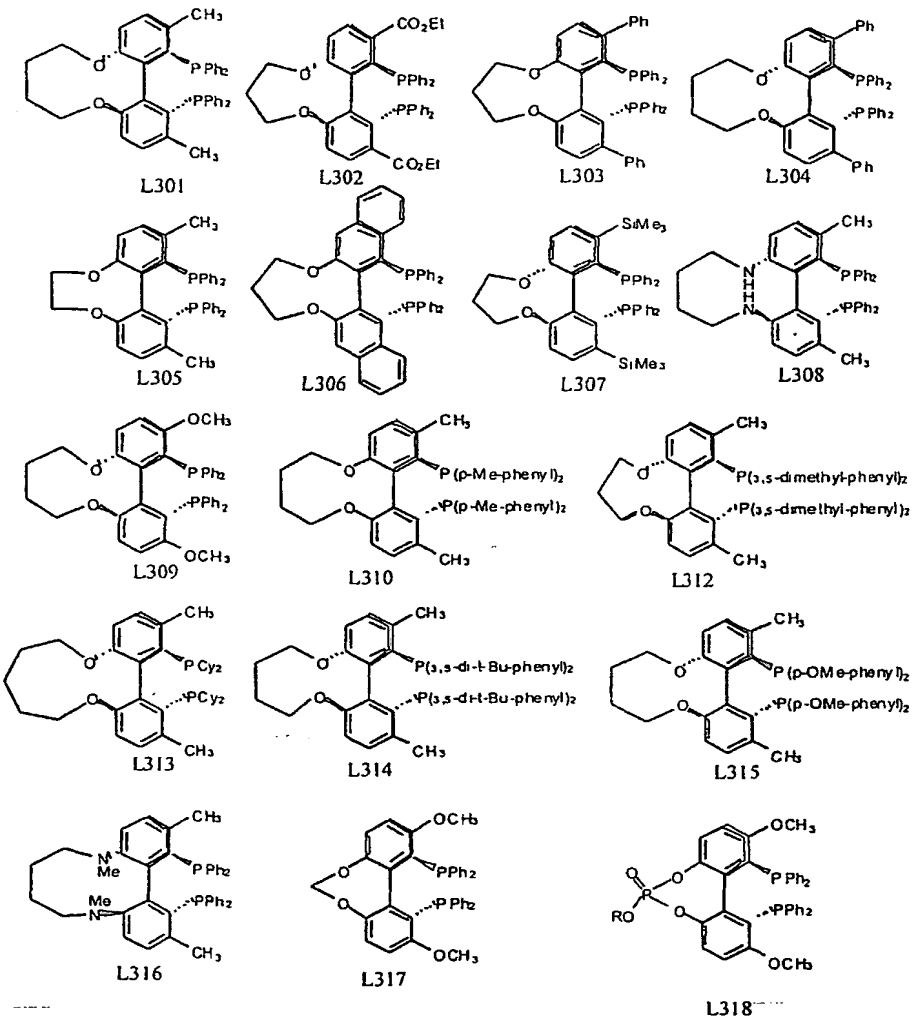

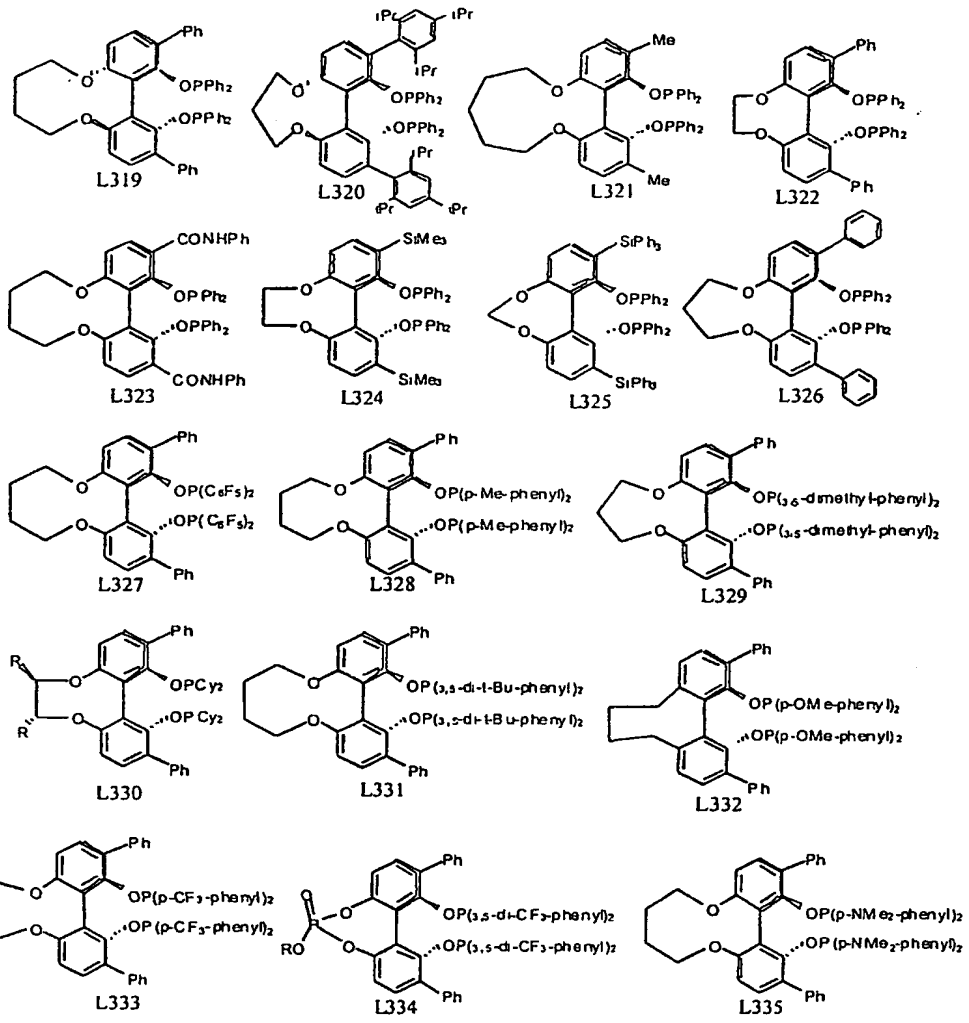

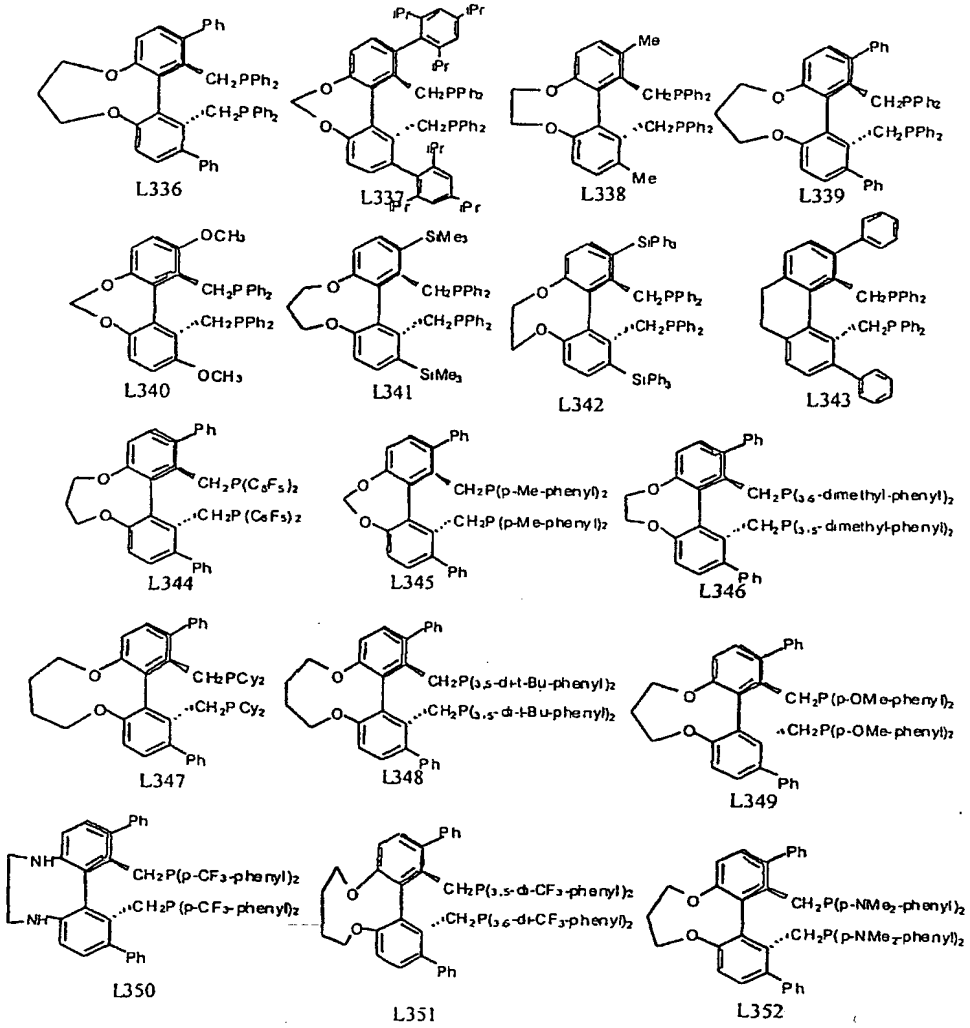

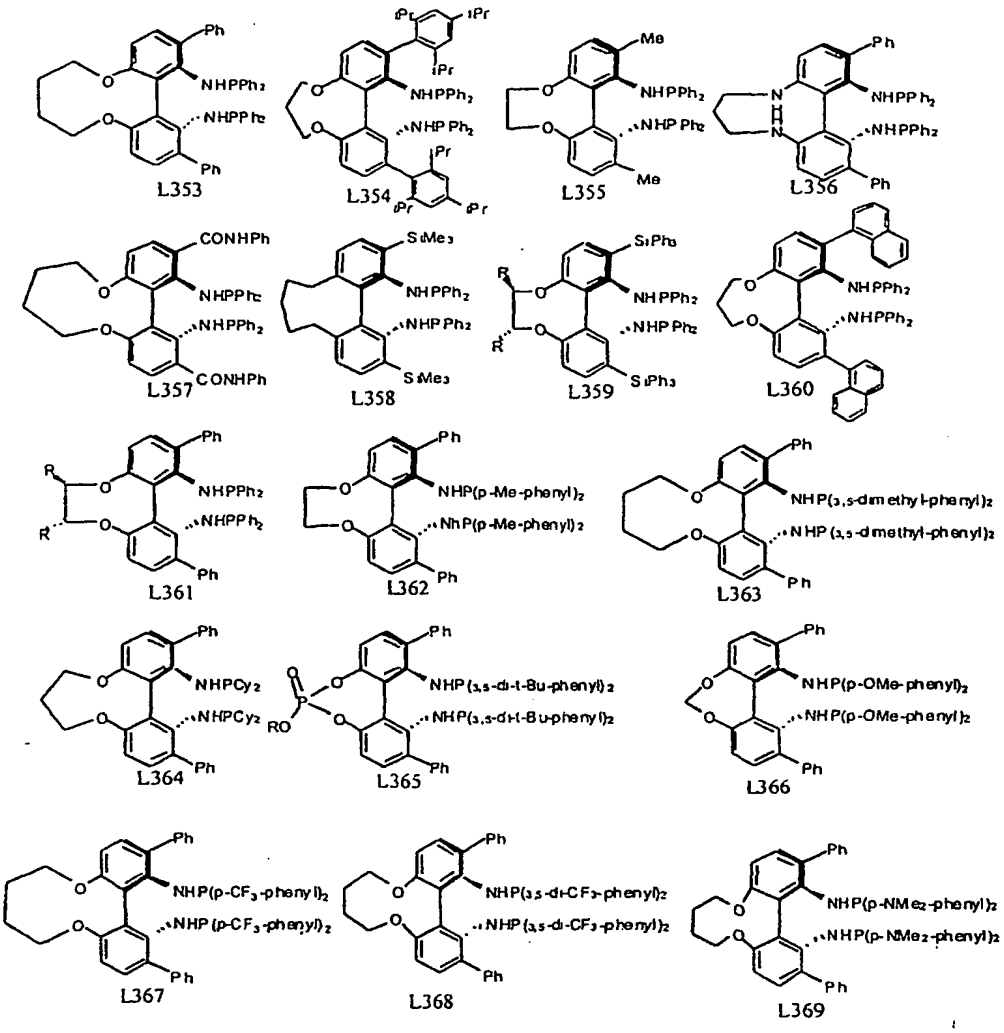

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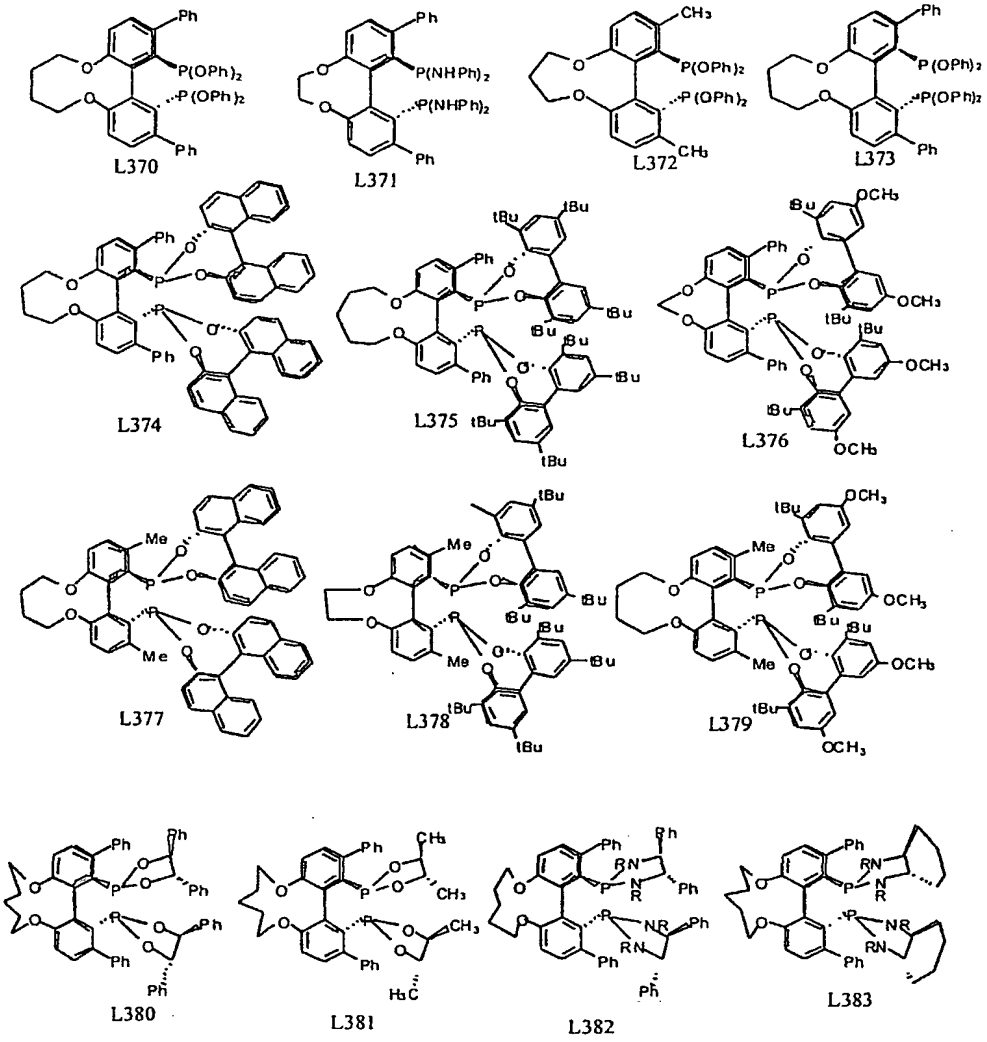

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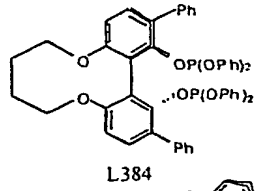
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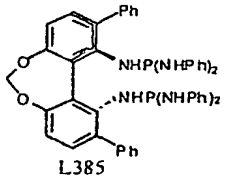
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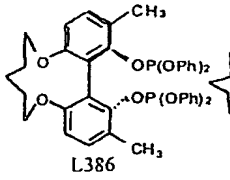
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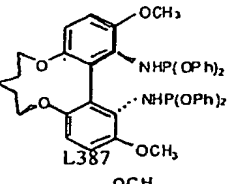
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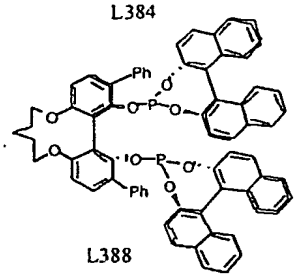
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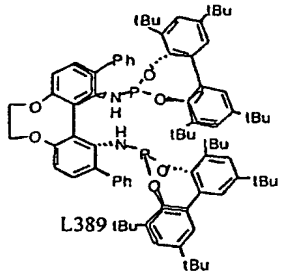
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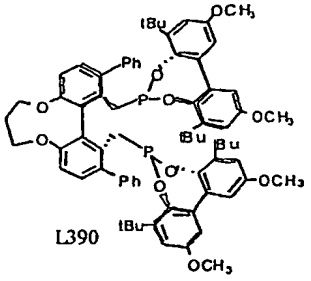
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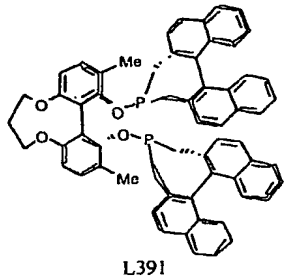
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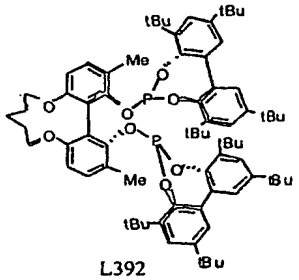
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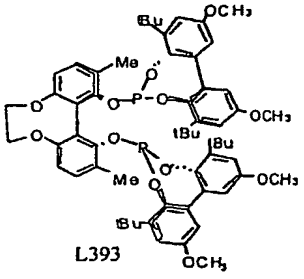
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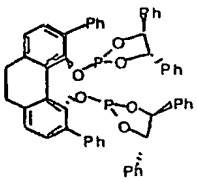
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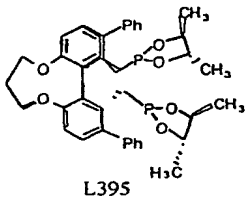
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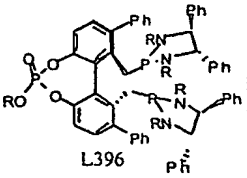
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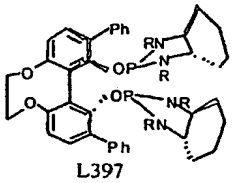
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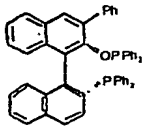
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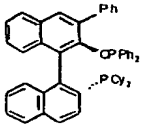
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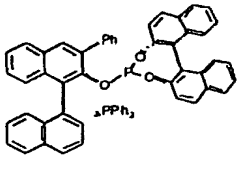
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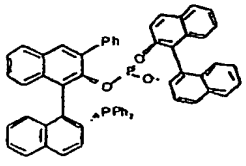
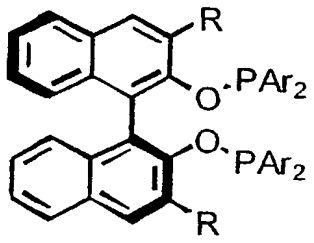
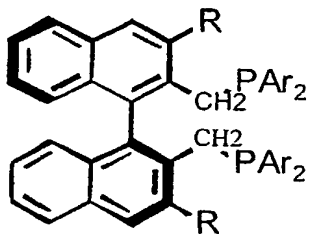

L401

15. The ligand of claim 1, represented by the formula:

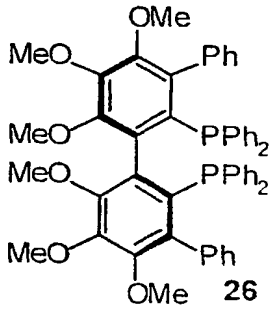


or



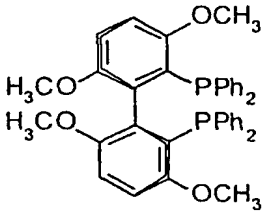
wherein each R is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl and SiR_3; and wherein each Ar is independently selected from the group consisting of: phenyl, substituted phenyl, aryl and substituted aryl.

16. The ligand of claim 1, represented by the formula:



26

17. The ligand of claim 1, represented by the formula:



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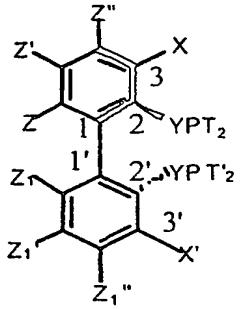
18. A catalyst prepared by a process comprising:

contacting a transition metal salt, or a complex thereof, and a ligand selected from the group consisting of compounds represented by the formula or its enantiomer:



wherein each X and X' is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

wherein each Z and Z_1 is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$; or wherein Z and Z_1 together form the bridging group A-B-A_1;

wherein each Z', Z", Z_1' and Z_1" is independently selected from the group consisting of: H, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$, or wherein Z' and Z together form the bridging group A'-B-A; Z' and Z together form a fused cycloaliphatic or aromatic group; Z_1 and Z_1' together form the bridging group A_1-B_1-A_1'; and/or Z_1 and Z_1' together form a fused cycloaliphatic or aromatic group;

wherein each A, A', A_1 and A_1' is independently selected from the group consisting of: O, CH_2, NH, NR, S, CO and a bond;

wherein each B and B_1 is independently selected from the group consisting of: linear, branched or cyclic alkylene of 1 to 6 carbon atoms, arylene of 6 to 12 carbon atoms, O, CH_2, NH, NR, S, CO, SO_2, P(O)R, P(O)OR, POR, SiR_2 and a bond;

wherein each T is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R", YR', YR", Y'R' and Y"R"; or wherein two T groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

wherein each T' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R", YR', YR", Y'R' and Y"R"; or wherein two T' groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

wherein each R, R' and R" is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, aralkyl and alkaryl of 1 to 22 carbon atoms; or wherein two R groups, two R' groups or two R" group together form an alkylene or arelene group; and

wherein each Y, Y' and Y" is independently selected from the group consisting of: O, CH_2, NH, S and a bond between carbon and phosphorus; with the proviso that when the Y group at the 2' position is a bond between carbon and phosphorus, X' is hydrogen.

19. The catalyst of claim 18, wherein said substituted alkyl has one or more substituents, each independently selected from the group consisting of: halogen, ester, ketone, carboxylic acid, hydroxy, alkoxy, aryloxy, thiol, alkylthio and dialkylamino.

20. The catalyst of claim 18, wherein said alkylene is selected from the group consisting of compounds represented by the formula: $-(CH_2)_n-$, where n is an integer in the range of from 1 to 8.

21. The catalyst of claim 18, wherein each of said aryl groups optionally has one or more substituents, each independently selected from the group consisting of: halogen, ester, ketone, sulfonate, phosphonate, hydroxy, alkoxy, aryloxy, thiol, alkylthiol, nitro, amino, vinyl, substituted vinyl, carboxylic acid, sulfonic acid and phosphine.

22. The catalyst of claim 18, wherein each of said arylene groups optionally has one or more substituents, each independently selected from the group consisting of: halogen, ester, ketone, sulfonate, phosphonate, hydroxy, alkoxy, aryloxy, thiol, alkylthiol, nitro, amino, vinyl, substituted vinyl, carboxylic acid, sulfonic acid and phosphine.

23. The catalyst of claim 18, wherein each of said arylene groups is independently selected from the group consisting of: 1,2-divalent phenyl, 2,2'-divalent-1,1'-biphenyl, 2,2'-divalent-1,1'-binaphthyl and ferrocene.

24. The catalyst of claim 18, wherein said ligand is a racemic mixture of enantiomers.

25. The catalyst of claim 18, wherein said ligand is a non-racemic mixture of enantiomers.

26. The catalyst of claim 18, wherein said ligand is one of the enantiomers.

27. The catalyst of claim 18, having an optical purity of at least 85% ee.

28. The catalyst of claim 18, having an optical purity of at least 95% ee.

29. The catalyst of claim 18, wherein said transition metal is selected from the group consisting of: Ag, Pt, Pd, Rh, Ru, Ir, Cu, Ni, Mo, Ti, V, Re and Mn.

30. The catalyst of claim 18, wherein said transition metal is selected from the group consisting of: Pt, Pd, Rh and Ru.

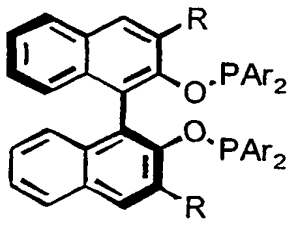
31. The catalyst of claim 18, wherein said transition metal salt, or complex thereof, is selected from the group consisting of: AgX; Ag(OTf); $Ag(OTf)_2$; AgOAc; $PtCl_2$; H_2PtCl_4; $Pd_2(DBA)_3$; $Pd(OAc)_2$; $PdCl_2(RCN)_2$; $(Pd(allyl)Cl)_2$; $Pd(PR_3)_4$; $(Rh(NBD)_2)X$; (Rh (NBD)Cl)$_2$; $(Rh(COD)Cl)_2$; $(Rh(COD)_2)X$; $Rh(acac)(CO)_2$; $Rh(ethylene)_2(acac)$; $(Rh(ethylene)_2Cl)_2$; $RhCl(PPh_3)_3$; $Rh(CO)_2Cl_2$; $RuHX(L)_2$(diphosphine), $RuX_2(L)_2$ (diphosphine), Ru(arene)X_2(diphosphine), Ru(aryl group)X_2; $Ru(RCOO)_2$(diphosphine); Ru(methallyl)2(diphosphine); Ru(aryl group)$X_2(PPh_3)_3$; Ru(COD)(COT); Ru(COD)(COT)X; RuX_2(cymen); $Ru(COD)_n$; Ru(aryl group)X_2(diphosphine); $RuCl_2$(COD); (Ru(COD)2)X; RuX_2(diphosphine); $RuCl_2(=CHR)(PR'_3)_2$; $Ru(ArH)Cl_2$; Ru(COD)(methallyl)$_2$; (Ir $(NBD)_2Cl)_2$; $(Ir(NBD)_2)X$; $(Ir(COD)_2Cl)_2$; $(Ir(COD)_2)X$; CuX $(NCCH_3)_4$; Cu(OTf); $Cu(OTf)_2$; Cu(Ar)X; CuX; $Ni(acac)_2$; NiX_2; $(Ni(allyl)X)_2$; Ni(COD)$_2$; $MoO_2(acac)_2$; $Ti(OiPr)_4$; $VO(acac)_2$; $MeReO_3$; MnX_2 and $Mn(acac)_2$; wherein each R and R' is independently selected from the group consisting of: alkyl or aryl; Ar is an aryl group; and X is a counteranion.

32. The catalyst of claim 31, wherein L is a solvent molecule and wherein said counteranion X is selected from the group consisting of: halogen, BF_4, B(Ar)4, wherein Ar is fluorophenyl or 3,5-di-trifluoromethyl-1-phenyl, ClO_4, SbF_6, PF_6, CF_3SO_3, RCOO and a mixture thereof.

33. The catalyst of claim 18, prepared in situ or as an isolated compound.

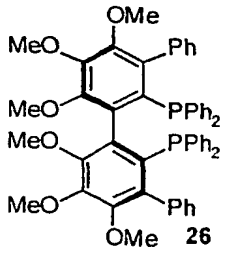
34. The catalyst of claim 18, wherein said transition metal salt, or a complex thereof is selected from the group consisting of: $[Rh(COD)Cl]_2$, $[Rh(COD)_2]X$, $[Ir(COD)Cl]_2$, $[Ir(COD)_2]X$, $Rh(acac)(CO)_2$, Ni(allyl)X, $Pd_2(dba)_3$, $[Pd(allyl)Cl]_2$, $Ru(RCOO)_2$(diphosphine), RuX_2(diphosphine), Ru(methylallyl)$_2$(diphosphine) and Ru(aryl)X_2(diphosphine), wherein X is selected from the group consisting of: BF_4, ClO_4, SbF_6, CF_3SO_3, Cl and Br; and wherein said ligand is selected from the group consisting of compounds represented by the formula:

(a)



wherein each R is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl and SiR_3; and wherein each Ar is independently selected from the group consisting of: phenyl, substituted phenyl, aryl and substituted aryl;

(b)



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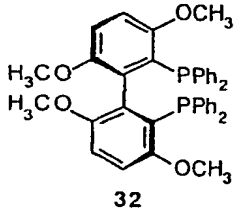

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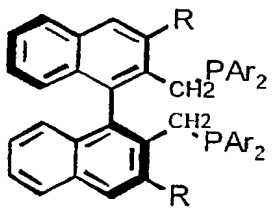
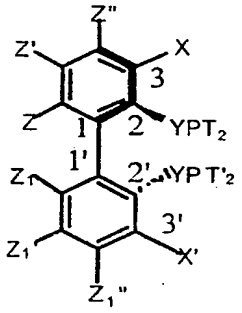
(d)



and a combination thereof.

35. A process for preparation of an asymmetric compound comprising:

contacting a substrate capable of forming an asymmetric product by an asymmetric reaction and a catalyst prepared by a process comprising: contacting a transition metal salt, or a complex thereof, and a ligand selected from the group consisting of compounds represented by the formula or its enantiomer:



wherein each X and X' is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$;

wherein each Z and Z_1 is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide,

SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$; or wherein Z and Z_1 together form the bridging group A-B-A_1;

wherein each Z', Z", Z_1' and Z_1" is independently selected from the group consisting of: H, alkyl, aryl, substituted alkyl, substituted aryl, OR, SR, NR_2, COOR, halide, SiR_3, $P(O)R_2$, $P(O)(OR)_2$ and $P(OR)_2$, or wherein Z' and Z together form the bridging group A'-B-A; Z' and Z together form a fused cycloaliphatic or aromatic group; Z_1 and Z_1' together form the bridging group A_1-B_1-A_1'; and/or Z_1 and Z_1' together form a fused cycloaliphatic or aromatic group;

wherein each A, A', A_1 and A_1' is independently selected from the group consisting of: O, CH_2, NH, NR, S, CO and a bond;

wherein each B and B_1 is independently selected from the group consisting of: linear, branched or cyclic alkylene of 1 to 6 carbon atoms, arylene of 6 to 12 carbon atoms, O, CH_2, NH, NR, S, CO, SO_2, P(O)R, P(O)OR, POR, SiR_2 and a bond;

wherein each T is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R", YR', YR", Y'R' and Y"R"; or wherein two T groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

wherein each T' is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, substituted aryl, alkoxide, aryloxide, R, R', R", YR', YR", Y'R' and Y"R"; or wherein two T' groups together form an alkylene, arylene, alkylenediamino, arylenediamino, alkelenedioxyl or arylenedioxyl;

wherein each R, R' and R" is independently selected from the group consisting of: alkyl, substituted alkyl, aryl, aralkyl and alkaryl of 1 to 22 carbon atoms; or wherein two R groups, two R' groups or two R" group together form an alkylene or arelene group; and

wherein each Y, Y' and Y" is independently selected from the group consisting of: O, CH_2, NH, S and a bond between carbon and phosphorus; with the proviso that when the Y group at the 2' position is a bond between carbon and phosphorus, X' is hydrogen.

36. The process of claim 35, wherein said asymmetric reaction is selected from the group consisting of: hydrogenation, hydride transfer, allylic alkylation, hydrosilylation, hydroboration, hydrovinylation, hydroformylation, olefin metathesis, hydrocarboxylation, isomerization, cyclopropanation, Diels-Alder reaction, Heck reaction, isomerization, Aldol reaction, Michael addition, epoxidation, kinetic resolution and [m+n] cycloaddition wherein m = 3 to 6 and n = 2.

37. The process of claim 36, wherein said transition metal is selected from the group consisting of:

Ag, Pt, Pd, Rh, Ru, Ir, Cu, Ni, Mo, Ti, V, Re and Mn.

38. The process of claim 36, wherein said asymmetric reaction is hydrogenation and said substrate is selected from the group consisting of: imine, ketone, ethylenically unsaturated compound, enamine, enamide and vinyl ester.

39. The process of claim 36, wherein said asymmetric reaction is a silver-catalyzed asymmetric [3 +2] cycloaddition of an azomethine ylide with a dipolarophile.

40. The process of claim 36, wherein said asymmetric reaction is a palladium-catalyzed allylic alkylation and said substrate is an allylic ester.

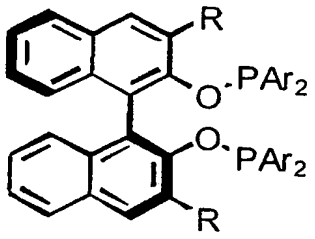
41. The process of claim 36, wherein said asymmetric palladium-catalyzed allylic alkylation reaction is a kinetic resolution reaction and said substrate is a racemic allylic ester.

42. The process of claim 36, wherein said asymmetric reaction is hydrogenation, said substrate is a beta-ketoester, said transition metal is Ru and said asymmetric compound is a beta-hydroxyester.

43. The process of claim 36, wherein said asymmetric reaction is hydrogenation, said substrate is an enamide, said transition metal is Ru and said asymmetric compound is a beta amino acid.

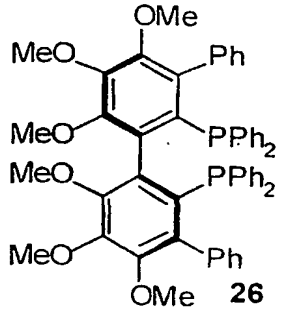
44. The process of claim 36, wherein said ligand is selected from the group consisting of compounds represented by the formula:

(a)



wherein each R is independently selected from the group consisting of: alkyl, aryl, substituted alkyl, substituted aryl and SiR_3; and wherein each Ar is independently selected from the group consisting of: phenyl, substituted phenyl, aryl and substituted aryl;

(b)



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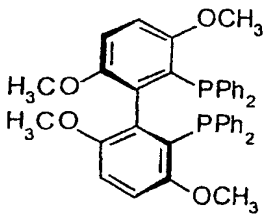
(c)



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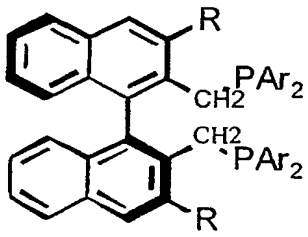
(d)



and a combination thereof.

45. The process of claim 44, wherein said asymmetric reaction is hydrogenation, said substrate is a beta-ketoester, said transition metal is Ru and said asymmetric compound is a beta-hydroxyester.

46. The process of claim 44, wherein said asymmetric reaction is hydrogenation, said substrate is an enamide, said transition metal is Ru and said asymmetric compound is a beta amino acid.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/43779

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C07F 9/06, 9/141, 9/50, 9/535, 9/655

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 558/70, 73, 76; 568/8, 12, 13, 14, 15, 16, 17; 556/13, 17, 18, 19, 20; 556/13, 17, 18, 19, 20; 502/162, 166

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P ---- A,P	Database Caplus on STN, Chemical abstracts, (Columbus OH, USA) CA:136:37900. SRIGES, W. et al. 'Method for the preparation of optically active trimethylactic acid and its esters', EP1160237, 05 December 2001.	1, 7 --- 2, 4, 8-10, 12-13, 16
X --- A	US 5,312,996 A (PACKETT) 17 May 1994, especially columns 5-10.	1, 7, 19, 25, 30-34 ---- 2,4, 8-10, 12-13, 16, 20, 22, 26-29, 35

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 22 MARCH 2002	Date of mailing of the international search report 16 APR 2002
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer Jayne Bridger JEAN F. VOLLANO Telephone No. (703) 308-1235

Form PCT/ISA/210 (second sheet) (July 1998)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/43779

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Database Caplus on STN, Chemical abstracts, (Columbus OH, USA) CA; 133:309942, (ZHANG et al) 'Synthesis of Chiral Bisphoshines with Tunable Bite Angles and Their Applications in Asymmetric Hydrogenation of .beta.ketoesters'. Journal of Organic Chemistry, 2000 65(19), pages 6223-6226.	1, 2, 4, 7-10, 12-16, 19, 20, 22, 25-35

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/43779

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II *Observations where unity of invention is lacking (Continuation of item 2 of first sheet)*

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
1, 2, 4, 7-10, 12-16, 19, 20, 22, 25-35 (in part)

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☒ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/43779

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

558/70, 73, 76; 568/8, 12, 13, 14, 15, 16, 17; 556/13, 17, 18, 19, 20; 556/13, 17, 18, 19, 20; 502/162, 166

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

CAS ONLINE, BEILSTEIN, EAST

search terms: 4 different structures drawn and searched, phosphine, catalyst, transition metal, phosphorous ester, diphosphine, Rh, Pd, Ru, Co, Re, Ir, Pt,

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s)1,2,4,7-13,16 (in part) drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is oxygen.
Group II, claim(s) 1,2,4,7-13,16 (in part) drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is CH2.
Group III , claim(s) 1,2,4,7-13, 14, 15, (in part) and 17, 18 (in full), drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is a bond.
Group IV, claim(s) 1, 2, 4,7-13, and 15 drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is NH.
Group V, claim(s) 1, 2, 7-13 , drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is a S.
Group VI, claim(s)1,2,4,7-13 (in part) drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is oxygen.
Group VII, claim(s) 1,2,4,7-13(in part) drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is CH2.
Group VIII , claim(s) 1,2,4, 7-13, drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is a bond.
Group IX, claim(s) 1, 2, 7-13, drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is NH.
Group X, claim(s) 1, 2,4, 7-13 , drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is a S.
Group XI, claim(s)1-13,15 (in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is oxygen.
Group XII, claim(s) 1-13, 15 (in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is CH2.
Group XIII , claim(s) 1, 2,4-13,15, (in part), drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is a bond.
Group XIV, claim(s) 1, 2,4-13, and 15 (in part) drawn to a ligand of the formula in claim 1 wherein the wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is NH.
Group XV, claim(s) 1, 2,4-13 , drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1

and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is a S.
Group XVI, claim(s)1,2,4-13 (in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is oxygen.
Group XVII, claim(s) 1,2,4-13(in part) drawn to a ligand of the formula in claim 1 wherein Z and Z' form A'BA and/or Z1 and Z1'form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is CH2.
Group XVIII , claim(s) 1,2,4-13, drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is a bond.
Group XIX, claim(s) 1, 2,4-13, drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form
A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is NH.
Group XX, claim(s) 1, 2, 4-13 , drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is a S.

Group XXI, claim(s)1-4,7-13(in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR and B is a carbon group the Z and Z1 form a ring wherein A1 and any A is NH or NR and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is oxygen.
Group XXII, claim(s) 1-4,7-13 (in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is CH2.
Group XXIII , claim(s) 1, 2,4,7-13 (in part), drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is a bond.
Group XXIV, claim(s) 1-4, 7-13, (in part) drawn to a ligand of the formula in claim 1 wherein the wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is NH.
Group XXV, claim(s) 1-4, 7-13 , drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is a S.
Group XXVI, claim(s)1-4,7-13 (in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is oxygen.
Group XXVII, claim(s) 1-4, 7-13(in part) drawn to a ligand of the formula in claim 1 wherein Z and Z' form A'BA and or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is CH2.
Group XXVIII , claim(s) 1-4,7-13, drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is a bond.
Group XXIX, claim(s) 1-4,7-13, drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is NH.
Group XXX, claim(s) 1-4, 7-13 , drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is

NH or NR and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is a S.

Group XXXI, claim(s)1-4,7-13(in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S and B is a carbon group the Z and Z1 form a ring wherein A1 and any A is S and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is oxygen.

Group XXXII, claim(s) 1-4,7-13 (in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is CH2.

Group XXXIII , claim(s) 1, 2,4,7-13 (in part), drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is a bond.

Group XXXIV, claim(s) 1-4, 7-13, (in part) drawn to a ligand of the formula in claim 1 wherein the wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is NH.

Group XXXV, claim(s) 1-4, 7-13 , drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is a S.

Group XXXVI, claim(s)1-4,7-13 (in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is oxygen.

Group XXXVII, claim(s) 1-4, 7-13(in part) drawn to a ligand of the formula in claim 1 wherein or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is CH2.

Group XXXVIII , claim(s) 1-4,7-13, drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is a bond.

Group XXXIX, claim(s) 1-4,7-13, drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S , and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is NH.

Group XL, claim(s) 1-4, 7-13 , drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is Sand Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is a S.

Group XLI, claim(s)1,2,4,7-13,16 (in part) drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.

Group XLII, claim(s) 1,2,4,7-13,16 (in part) drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is CH2.

Group XLIII , claim(s) 1,2,4,7-13, 14, 15, (in part) and 17, 18 (in full), drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is a bond.

Group XLIV, claim(s) 1, 2, 4,7-13, and 15 drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.

Group XLV, claim(s) 1, 2, 7-13 , drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, T at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.

Group XLVI, claim(s)1,2,4,7-13 (in part) drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, at least one T is selected from phosphorus or silicon groups and the other T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.

Group XLVII, claim(s) 1,2,4,7-13(in part) drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and the other T is a heteroring with oxygen or nitrogen heteroatoms and Y is CH2.

Group XLVIII , claim(s) 1,2,4, 7-13, drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not

heterorings, one T is selected from phosphorus or silicon groups and the other T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a bond.
Group XLIX, claim(s) 1, 2, 7-13, drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, at least one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.
Group L, claim(s) 1, 2,4, 7-13 , drawn to a ligand of the formula in claim 1 wherein the Zs and Xs are not heterorings, one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.
Group LI, claim(s)1-13,15 (in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.
Group LII, claim(s) 1-13, 15 (in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is CH_2.
Group LIII , claim(s) 1, 2,4-13,15, (in part), drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is a bond.
Group LIV, claim(s) 1, 2,4-13, and 15 (in part) drawn to a ligand of the formula in claim 1 wherein the wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.
Group LV, claim(s) 1, 2,4-13 , drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.
Group LVI, claim(s)1,2,4-13 (in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.
Group LVII, claim(s) 1,2,4-13(in part) drawn to a ligand of the formula in claim 1 wherein Z and Z' form A'BA and/or Z1 and Z1'form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, one T is selected from phosphorus or silicon groups or phosphorus or silicon groups one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is CH_2.
Group LVIII , claim(s) 1,2,4-13, drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, one T is selected from phosphorus or silicon groups at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a bond.
Group LIX, claim(s) 1, 2,4-13, drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form
A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.
Group LXX, claim(s) 1, 2, 4-13 , drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.

Group LXXI, claim(s)1-4,7-13(in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR and B is a carbon group the Z and Z1 form a ring wherein A1 and any A is NH or NR and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.
Group LXXII, claim(s) 1-4,7-13 (in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is CH_2.
Group LXXIII , claim(s) 1, 2,4,7-13 (in part), drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a

carbon group and A is NH or NR and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is a bond.
Group LXXIV, claim(s) 1-4, 7-13, (in part) drawn to a ligand of the formula in claim 1 wherein the wherein the Z and Z' form A'B A and/or Z1 and Z1'form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.
Group LXXV, claim(s) 1-4, 7-13 , drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.
Group LXXVI, claim(s)1-4,7-13 (in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, one T is selected from phosphorus or silicon groups and at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.
Group LXXVII, claim(s) 1-4, 7-13(in part) drawn to a ligand of the formula in claim 1 wherein Z and Z' form A'BA and or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, one T is selected from phosphorus or silicon groups or phosphorus or silicon groups at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is CH2.
Group LXXVIII , claim(s) 1-4,7-13, drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus one T is selected from phosphorus or silicon groups and Y is a bond.
Group LXXIX, claim(s) 1-4,7-13, drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings,one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.
Group LXXX, claim(s) 1-4, 7-13 , drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.
Group LXXXI, claim(s)1-4,7-13(in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S and B is a carbon group the Z and Z1 form a ring wherein A1 and any A is S and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.
Group LXXXII, claim(s) 1-4,7-13 (in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is CH2.
Group LXXXIII , claim(s) 1, 2,4,7-13 (in part), drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is a bond.
Group LXXXIV, claim(s) 1-4, 7-13, (in part) drawn to a ligand of the formula in claim 1 wherein the wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings,at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.
Group LXXXV, claim(s) 1-4, 7-13 , drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.
Group LXXXVI, claim(s)1-4,7-13 (in part) drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.
Group LXXXVII, claim(s) 1-4, 7-13(in part) drawn to a ligand of the formula in claim 1 wherein or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is CH2.
Group LXXXVIII , claim(s) 1-4,7-13, drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A

and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a bond.

Group LXXXIX, claim(s) 1-4,7-13, drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.

Group XC, claim(s) 1-4, 7-13 , drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is Sand Xs are not heterorings, one T is selected from phosphorus or silicon groups and at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.

Group XCI, claim(s)19, 20,22, 25-35 (in part) drawn to a transition metal catalyst of the formula in claim 19 and wherein the Zs and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is oxygen with a transition metal.

Group XCII, claim(s) 19,20,22, 25-35 (in part) drawn to a catalyst of the formula in claim 19 wherein the Zs and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is CH2 with a transition metal.

Group XCIII , claim(s)19,20,22, 25-35 (in part) , drawn to a catalyst of the formula in claim 1 wherein the Zs and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is a bond with a transition metal.

Group XCIV, claim(s)19,20,22, 25-35 (in part) drawn to a ligand of the formula in claim 19 wherein the Zs and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is NH with a transition metal .

Group XCV, claim(s)19,20,22, 25-35 (in part) , drawn to a transition metal catalyst of the formula in claim 19 wherein the Zs and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is a S.

Group XCVI, claim(s)19,20,22, 25-35(in part) drawn to a transition metal catalyst of the formula in claim 19 wherein the Zs and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is oxygen.

Group XCVII, claim(s) 19,20,22, 25-35 (in part) drawn to a transition metal catalyst of the formula in claim 19 wherein the Zs and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is CH2.

Group XCVIII , claim(s) 19,20,22, 25-35 (in part) drawn to a transition metal catalyst of the formula in claim 19 wherein the Zs and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is a bond.

Group XCIX, claim(s) 19,20,22, 25-35 (in part), drawn to a transition metal catalyst of the formula in claim 19 wherein the Zs and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is NH.

Group C, claim(s)19,20,22, 25-35 (in part), drawn to a transition metal catalyst the formula in claim 19 wherein the Zs and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is a S.

Group CI, claim(s)19-35 drawn to a transition metal catalyst of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is oxygen.

Group CII, claim(s) 19-35(in part) drawn to a transition metal catalyst the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is CH2.

Group CIII , claim(s) 19-35, drawn to a transition metal catalyst of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is a bond.

Group CIV, claim(s) 19,20,22, 25-35 (in part) drawn to a transition metal catalyst of the formula in claim 19 wherein the wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is NH.

Group CV, claim(s) 19,20,22, 25-35 (in part) , drawn to a ligand of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is a S.

Group CVI, claim(s) 19,20,22, 25-35 (in part) drawn to a ligand of the formula in claim 19 wherein the Z and Z' form

A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is oxygen.

Group CVII, claim(s) 19,20,22, 25-35 (in part) drawn to a transition metal catalyst of the formula in claim 19 wherein Z and Z' form A'BA and/or Z1 and Z1'form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is CH2.

Group CVIII , claim(s) 19,20,22, 25-35 , drawn to a transition metal catalyst of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is a bond.

Group CIX, claim(s) 19,20,22, 25-35(in part), drawn to a transition metal catalyst of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is NH.

Group CX, claim(s) 19,20,22, 25-35 (in part) , drawn to a transition metal catalyst of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is a S.

Group CXI, claim(s)19-35(in part) drawn to a transition metal catalysts of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR and B is a carbon group the Z and Z1 form a ring wherein A1 and any A is NH or NR and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is oxygen.

Group CXII, claim(s) 19-35 (in part) drawn to a transition metal catalyst of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is CH2.

Group CXIII , claim(s) 19,20,22, 25-35 (in part), drawn to a transition metal catalyst of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is a bond.

Group CXIV, claim(s) 19-35 (in part) drawn to a transition metal catalyst of the formula in claim 19 wherein the wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is NH.

Group CXV, claim(s)19-35 , drawn to a transition metal catalyst of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is a S.

Group CXVI, claim(s)19-35(in part) drawn to a ligand of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is oxygen.

Group CXVII, claim(s)19-35(in part) drawn to a transition metal catalysts of the formula in claim 19 wherein Z and Z' form A'BA and or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is CH2.

Group CXVIII , claim(s) 19-35, drawn to a transition metal catalyst of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is a bond.

Group CXIX, claim(s) 19-35, drawn to a transition metal catalyst of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is NH.

Group CXX, claim(s) 19-35 , drawn to a transition metal catalyst of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is a S.

Group CXXI, claim(s) 19-35(in part) drawn to a transition metal catalyst (i.e. TMC) of the formula in claim 19

wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S and B is a carbon group the Z and Z1 form a ring wherein A1 and any A is S and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is oxygen.

Group CXXII, claim(s) 19-35 (in part) drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is CH2.

Group CXXIII , claim(s) 19,20,22, 25-35 (in part), drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and at least one Y is a bond.

Group CXXIV, claim(s) 19-35(in part) drawn to a TMC of the formula in claim 1 wherein the wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is NH.

Group CXXV, claim(s) 19-35, drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings or phosphorus or silicon groups and Y is a S.

Group CXXVI, claim(s) 19-35(in part) drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is oxygen.

Group CXXVII, claim(s)19-35(in part) drawn to a TMC of the formula in claim 19 wherein or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is CH2.

Group CXXVIII , claim(s) 19-35, drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and Y is a bond.

Group CXXIX, claim(s) 19-35, drawn to a TMC of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is NH.

Group CXXX, claim(s) 19-35, drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is Sand Xs are not heterorings, Ts are not heterorings but at least one T is selected from phosphorus or silicon groups and Y is a S.

Group CXXXI, claim(s)19,20,22, 25-35(in part) drawn to a TMC of the formula in claim 19 wherein the Zs and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.

Group CXXXII, claim(s) 19,20,22, 25-35 (in part) drawn to a TMC of the formula in claim 19 wherein the Zs and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is CH2.

Group CXXXIII , claim(s) 19,20,22, 25-35 (in part), drawn to a ligand of the formula in claim 19 wherein the Zs and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is a bond.

Group CXXXIV, claim(s) 19,20,22, 25-35 (in part) drawn to a ligand of the formula in claim 19 wherein the Zs and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.

Group CXXXV, claim(s) 19,20,22, 25-35 (in part) , drawn to a TMC of the formula in claim 19 wherein the Zs and Xs are not heterorings, T at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.

Group CXXXVI, claim(s)19,20,22, 25-35 (in part) drawn to a TMC of the formula in claim 19 wherein the Zs and Xs are not heterorings, at least one T is selected from phosphorus or silicon groups and the other T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.

Group CXXXVII, claim(s)19,20,22, 25-35(in part) drawn to a TMC of the formula in claim 19 wherein the Zs and Xs are not heterorings, at least one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and the other T is a heteroring with oxygen or nitrogen heteroatoms and Y is CH2.

Group CXXXVIII , claim(s) 19,20,22, 25-35, drawn to a TMC of the formula in claim 19 wherein the Zs and Xs are not heterorings, one T is selected from phosphorus or silicon groups and the other T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a bond.

Group CXXXIX, claim(s) 19,20,22, 25-35 (in part), drawn to a TMC of the formula in claim 19 wherein the Zs and Xs

are not heterorings, at least one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.
Group CXL, claim(s) 19,20,22, 25-35 , drawn to a TMC of the formula in claim 19 wherein the Zs and Xs are not heterorings, one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.
Group CXLI, claim(s)19-35(in part) drawn to a ligand of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.
Group CXLII, claim(s)19-35 (in part) drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is CH2.
Group CXLIII , claim(s) 19,20,22, 25-35, (in part), drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is a bond.
Group CXLIV, claim(s) 19,20,22, 25-35 (in part) drawn to a TMC of the formula in claim 19 wherein the wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.
Group CXLV, claim(s)19,20,22, 25-35 (in part), drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.
Group CXLVI, claim(s)19,20,22, 25-35 (in part) drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.
Group CXLVII, claim(s) 19,20,22, 25-35(in part) drawn to a TMC of the formula in claim 19 wherein Z and Z' form A'BA and/or Z1 and Z1'form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, one T is selected from phosphorus or silicon groups or phosphorus or silicon groups one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is CH2.
Group CXLVIII , claim(s) 19,20,22, 25-35 (in part), drawn to a ligand of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, one T is selected from phosphorus or silicon groups at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a bond.
Group CXLIX, claim(s) 19,20,22, 25-35, drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.
Group CL, claim(s) 19,20,22, 25-35 (in part) , drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is oxygen and B is a carbon group or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is oxygen and Xs are not heterorings, one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.

Group CLI, claim(s)19-35(in part) drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR and B is a carbon group the Z and Z1 form a ring wherein A1 and any A is NH or NR and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.
Group CLII, claim(s) 19-35 (in part) drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is CH2.
Group CLIII , claim(s) 19-35 (in part), drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is a bond.

Group CLIV, claim(s) 19-35 (in part) drawn to a TMC of the formula in claim 19 wherein the wherein the Z and Z' form A'B A and/or Z1 and Z1'form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.
Group CLV, claim(s) 19-35, drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.
Group CLVI, claim(s)19-35 (in part) drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, one T is selected from phosphorus or silicon groups and at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.
Group CLVII, claim(s) 19-35(in part) drawn to a TMC of the formula in claim 1 wherein Z and Z' form A'BA and or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, one T is selected from phosphorus or silicon groups or phosphorus or silicon groups at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is CH2.
Group CLVIII , claim(s) 19-35 (in part), drawn to a TMC of the formula in claim 1 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus one T is selected from phosphorus or silicon groups and Y is a bond.
Group CLIX, claim(s) 19-35 (in part), drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or NR or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings,one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.
Group CLX, claim(s) 19-35 (in part), drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is NH or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is NH or NR and Xs are not heterorings, one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.
Group CLXI, claim(s)19-35 (in part) drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S and B is a carbon group the Z and Z1 form a ring wherein A1 and any A is S and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.
Group CLXII, claim(s)19-35 (in part) drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is CH2.
Group CLXIII , claim(s) 19-35 (in part), drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and at least one Y is a bond.
Group CLXIV, claim(s) 19-35, (in part) drawn to a TMC of the formula in claim 19 wherein the wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings,at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.
Group CLXV, claim(s)19-35(in part) , drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.
Group CLXVI, claim(s)19-35 (in part) drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is oxygen.
Group CLXVII, claim(s) 19-35(in part) drawn to a TMC of the formula in claim 19 wherein or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, one T is selected from phosphorus or silicon groups or phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is CH2.
Group CLXVIII , claim(s)19-35 (in part) drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, one T is selected from phosphorus or silicon groups or phosphorus or silicon groups

and at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a bond.

Group CLXIX, claim(s) 19-35 (in part), drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is S and Xs are not heterorings, one T is selected from phosphorus or silicon groups and one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is NH.

Group CLXX, claim(s) 19-35 , drawn to a TMC of the formula in claim 19 wherein the Z and Z' form A'B A and/or Z1 and Z1' form A'1B1A1 and any A is S or Z and Z1 form a ring of ABA1 wherein B is a carbon group and A is Sand Xs are not heterorings, one T is selected from phosphorus or silicon groups and at least one T is a heteroring with oxygen or nitrogen heteroatoms making a ring with the phosphorus and Y is a S.

Group CLXX1, claim(s) 36-47 a process for the preparation of an asymmetric compound. If this group is elected a transition metal catalysts from the above groups should be selected and a reaction (e.g. hydrogenation or hydride transfer) should also be selected.

It is noted that roman numerals LX-LXIX were not used as group numbers.

The inventions listed do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The only common core in all the ligand claims is a biphenyl ring. This is not a substantial core nor applicants contribution to the art. All the ligands only contain in common a biphenyl group and therefore there is no special technical feature combining the ligands. The transition metal catalysts are a variety of transition metals(which could have also been placed in different groups due to the unique metal portion)which have different chelates attached to them. Again the only common core is the biphenyl ring. There is no special technical feature which unites these transition metal catalysts. The ligand groups and the transition metal catalysts do not fit any category under unity of invention. Thus there is a lack of unity of invention in the Groups. The method of use of the transition metal catalysts which has been placed in its own group has many method of use. There are variations of asymmetric synthesis and as such they do not fit in the category under unity of invention of a compound (transition metal compound) and a method of use. There are various methods of use and not "a" method. Therefore if a transition metal compound Group is chosen then there can also be a choice of a method of use of the transition metal compound as part of that group.